Vol. 2 SEPTEMBER, 1919 No. 9

Journal

—OF THE—

American Ceramic Society

A Monthly Journal devoted to the Arts and Sciences Related to the Silicate Industries.

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Published Monthly by the
AMERICAN CERAMIC SOCIETY

Publication Office
211 Church St., Easton, Pa.

Editorial Office
Rutgers College, New Brunswick, N. J.

SIX DOLLARS PER YEAR (Foreign Postage Additional) *SINGLE NUMBERS, SIXTY CENTS*

Entered as second-class matter, July 15, 1918, at the post office at Easton, Pa., under the Act of March 3, 1879.

Acceptance for mailing at special rate of postage provided for in section 1103, Act of October 3, 1917, authorized August 16, 1918.

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JOURNAL OF THE AMERICAN CERAMIC SOCIETY VOL. 2, NO. 9, SEPTEMBER, 1919

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JOURNAL
OF THE
AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 2 **September, 1919** **No. 9**

EDITORIALS.

CERAMIC RESEARCH.

Considerable emphasis has been placed of late upon the need of more accurate methods and data for conducting ceramic researches. The value of many of the ceramic researches which have been published in the literature is open to question owing to the fact that the measurements were not accurately made—not through carelessness on the part of the investigator but owing to his lack of accurate measuring instruments and fundamental data in outlining and making the tests.

The results secured in a great many of our investigations have been comparative only and have not been based upon fundamental laws and constants. This applies particularly to investigations of glazes, which have been for the most part empirical. In attempting to apply the results and conclusions drawn from investigations of this kind, we are too often confronted by the fact that statements made and general conclusions drawn are not borne out in similar investigations made under slightly different conditions. Our ceramic bodies, glazes and glasses are complicated in the extreme and working as we are with impure materials it is not strange that the conclusions drawn have often been too sweeping.

Fundamental data as to the properties of ceramic materials are gradually being made available but the remaining fields to be covered are of very large extent. But few of our ceramic laboratories have facilities for the determination of the data required—in fact, many of our investigations fall outside the

field of the technical ceramist and should be conducted by trained physicists in well-equipped physical laboratories. This applies particularly to investigations involving the measurement of coefficients of expansion, thermal conductivity, dielectric strength, etc.

As an illustration of the need of reliable data of this kind, let us consider that property, so vital to many of our ceramic products, "resistance to temperature changes." We know in a general way that this property is dependent to a certain extent on coefficient of expansion, thermal conductivity, mechanical strength, etc. We do not know, however, the relative importance of these properties and, if so, we do not have available sufficient reliable data to develop a product having this property. The only alternative is to make a series of comparative tests, trusting to good fortune that a product having the desired resistance to temperature changes will be secured.

Let us encourage to the utmost the compilation of fundamental data pertaining to ceramic research!

CERAMIC MUSEUM.

The plans which are under way for the establishment of a museum for displaying the historical growth and development of the ceramic industry in the State of New Jersey gives rise to the question whether, in the not too distant future, it will be feasible to establish a national ceramic museum.

In our colleges and universities and in some of our national museums we have fairly creditable ceramic exhibits, but these are not complete by any means and nowhere has an attempt been made to depict the history and development of the many branches of the industry which have become firmly established in this country. A well established national museum would be a source of pride and gratification to the present and future generations of ceramists and of great value in depicting the economic value of this branch of our industries.

ORIGINAL PAPERS AND DISCUSSIONS

THE WHITE CLAY POSSIBILITIES OF PENNSYLVANIA.

By Richard R. Hice.

We need say nothing at this time regarding the importance of what we generally designate as the "White Clay Industry." The demand for the higher-grade clays has resulted in a somewhat extensive reconnaissance of the white-clay deposits of the State of Pennsylvania, and a somewhat detailed investigation of two of the more promising horizons, which will be followed by studies elsewhere.

Disregarding the kaolins of southeastern Pennsylvania, which have been extensively worked in the past, the result of this study shows the occurrence of white clays within the sedimentary rocks at four distinct horizons. The studies have not as yet been sufficiently advanced to determine how closely conditions at these several horizons resemble one another, but it is probable that the conditions are not the same at all of them. The clays at some points have apparently been derived from the decomposition of shales and at other places from sandstones or limestones.

Geological Occurrence.

Clays in Cambrian Formation.—If we examine the geological column in Pennsylvania we will find it fairly well represented by the accompanying section (Fig. 1) taken from the reports of the Second Geological Survey of Pennsylvania. Overlying the Pre-Cambrian rocks, in the southeastern part of the State, occur the Cambrian formations, and in this series is found the Chickies Quartzite. This is a formation occurring in a number of places in southeastern Pennsylvania (Map No. 1) extending from a point on the Maryland line, southwest of Gettysburg, in a general

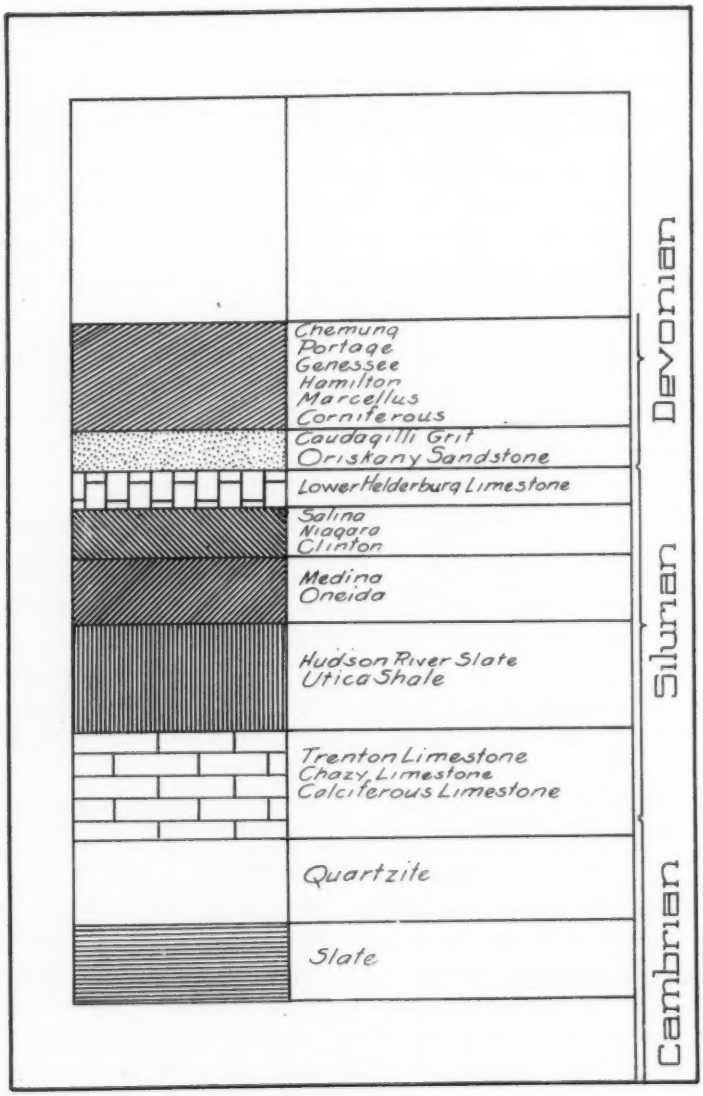
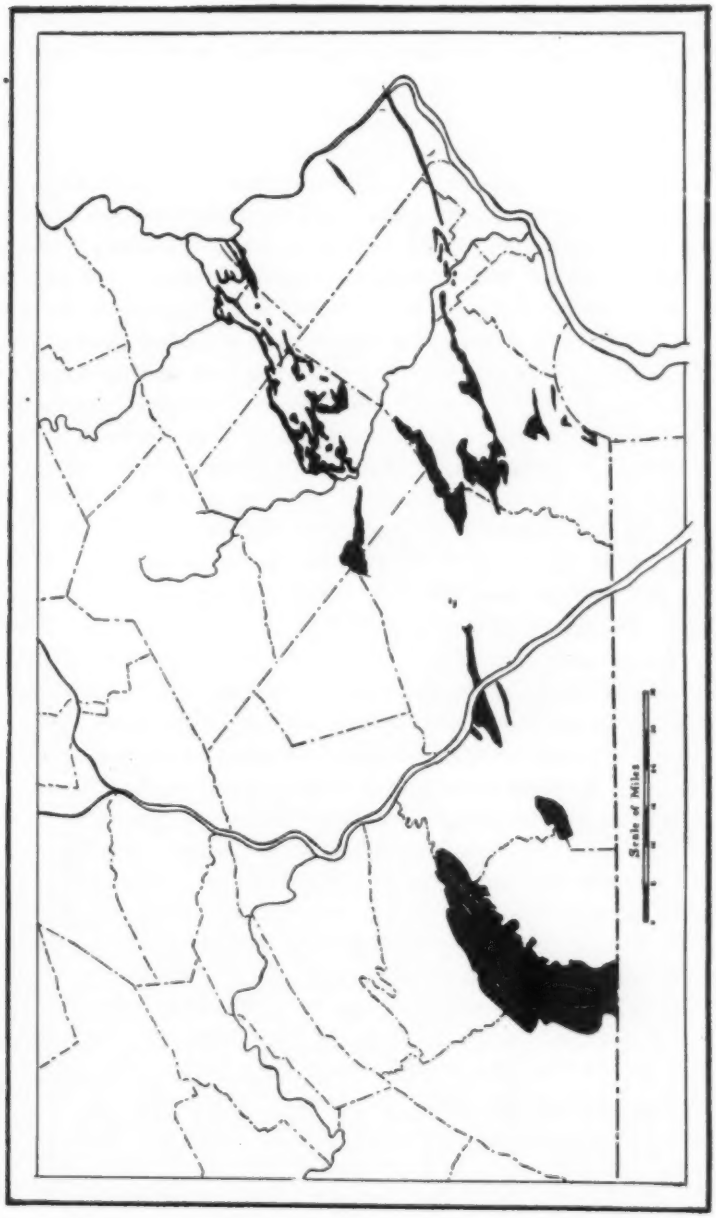

Chemung
Portage
Genessee
Hamilton
Marcellus
Corniferous
Caudagilli Grit
Oriskany Sandstone
Lower Helderburg Limestone
Salina
Niagara
Clinton
Medina
Oneida
Hudson River Slate
Utica Shale
Trenton Limestone
Chazy Limestone
Calciferous Limestone
Quartzite
Slate
Devonian
Silurian
Cambrian

FIG. 1.



MAP No. 1—Distribution of Cambrian Quartzite in Pennsylvania

northeasterly direction to the Delaware River, a little south of Easton. In this region there are many places where the quartzite is not found, due to the irregular and complicated structure which has been impressed on these old rocks and to erosion which has in many places carried away large areas.

The belt of Cambrian quartzite extends from the Maryland line northeasterly, passing near Mount Holly Springs, through Dillsburg, crossing the Schuylkill River near Reading, touching the Lehigh River near Allentown and Bethlehem, and passing out of the State a few miles south of Easton. West of the Susquehanna River the formation extends as a wide and quite regular mass, while east of Reading it is quite irregular in its occurrence.

Southward from the area described is a second series of exposures reaching from a little southwest of York, through Columbia, where it crosses the Susquehanna River, passing eastward through Honeybrook, Coatesville, Norristown, and reaching the Delaware northwest of Trenton in a narrow band. These occurrences of the Cambrian occur in what may be described as three blocks, the most westerly extending from a point in Lancaster County southwesterly, through Columbia and York; the central area extending from northeastern Lancaster County, near Honeybrook, to a point near Norristown; and the third area extending from Norristown to the Delaware River. Still another occurrence crosses south of Coatesville, adjacent to the Delaware state line. This occurrence is of small extent.

Adjoining the outcrop of the quartzite at many places occurs the limestone series at the base of the Silurian (we are using the names as described and published in the reports of the Second Geological Survey of Pennsylvania) and the clay seems to occur at or near the contact of the quartzite with the overlying limestones.

The best known occurrence of clays at this horizon is, perhaps, in the Mt. Holly Springs region, in Cumberland County, and several descriptions have been published on the clays there. There are two distinct localities near Mt. Holly. The first is a little southwest of Mt. Holly on a small stream known as Furnace Run. For several miles along this stream the overlying limestone occurs, and it is along this portion of the valley that the white clays are found. The clay is quite closely associated with the

iron ores which have been mined in the past in this area. A second occurrence of white clay, near Mt. Holly, is east of the town, also at or close to the point of contact of the limestone and quartzite. It is also being mined at this locality. West of Mt. Holly, at the same general horizon, white clays are reported, but as yet have not been investigated.

Another occurrence of white clay in this same general region is west of Dillsburg. The maps of the Second Geological Survey do not show the limestones as being found here in the same valley as the clay. However, the clays are also closely associated with the iron ores and the old iron-ore mines, and probably the limestones are present. At this point the clay has been opened but was not being shipped at the time of our visit.

Passing northeasterly to and beyond Reading, but very little is known of the clay at this horizon, as it has not been examined as yet.

In northeastern Lancaster County, at Narvon, near Honeybrook, quite extensive clay deposits occur at the same general horizon. Here the clay has a very extensive development, and while not apparently of as good quality as the clay in the Mt. Holly region, it is quite extensively mined.

Clay is also known to occur at this same general horizon in the neighborhood of Coatesville, and northeast, in the neighborhood of Frazer, where, from the little knowledge we now have, it is apparently of much better quality than near Narvon.

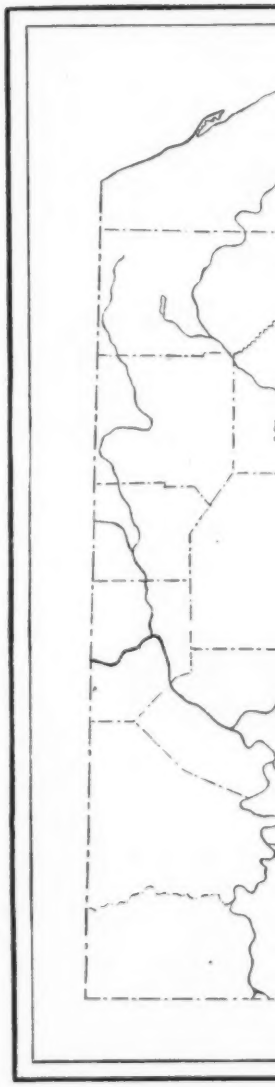
A reconnaissance survey was made last summer over part of this region in company with Dr. H. Ries and Dr. F. B. Peck. The finding of clays at a number of points at this horizon rather indicates that they will be found at other places, and considering the relatively high grade of the deposits now known, it may at least be expected that at some points clays will be found of a better quality. Since making the survey of last summer, Dr. Ries reports the receipt of a sample of clay from one point which developed a good color when fired at cone 10.

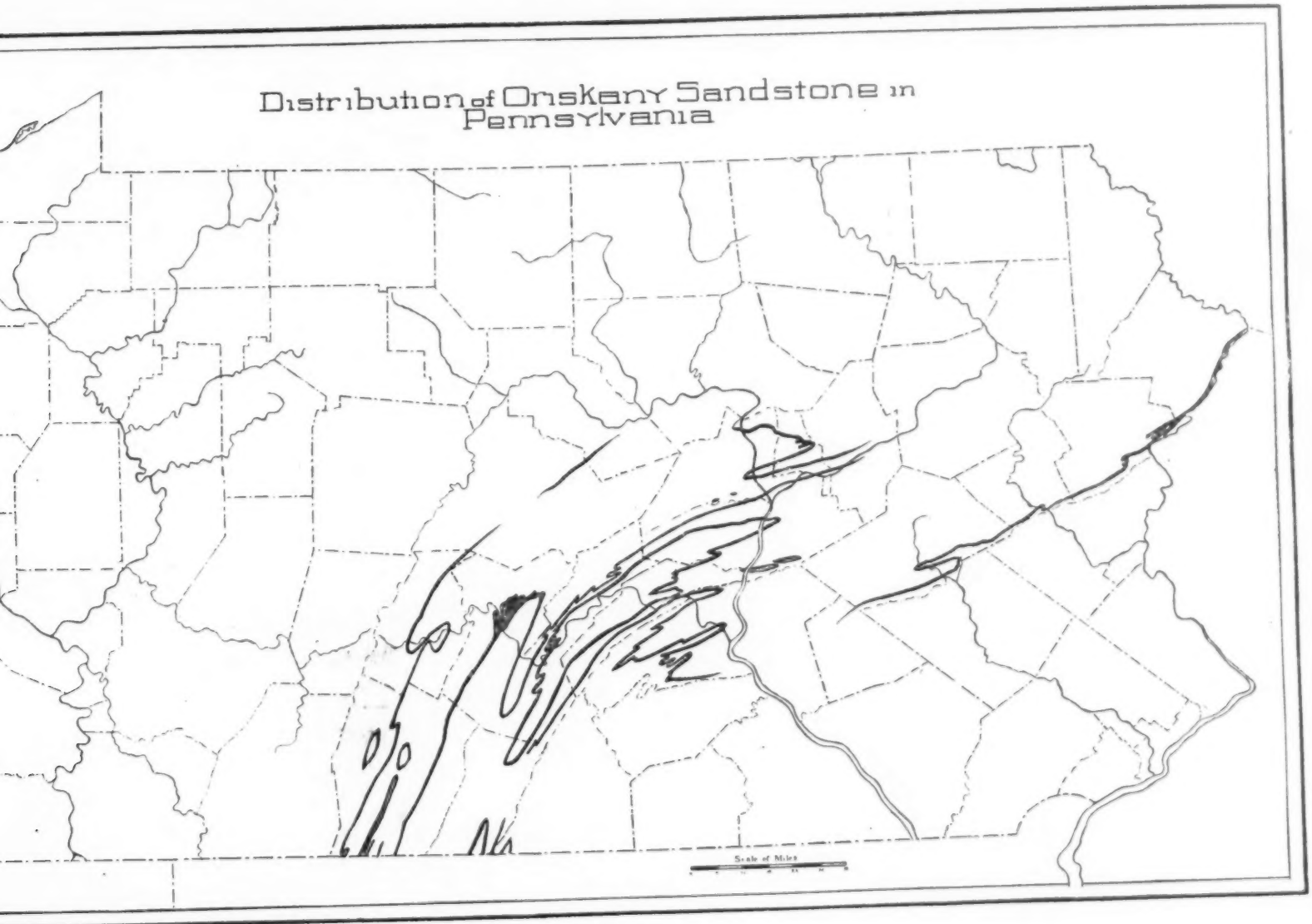
It is expected that a somewhat detailed study of at least a portion of the possibilities suggested will be made during the coming summer.

Clays in the Gatesburg Sandstone.—Passing higher into the Cambrian formations, we find in Huntingdon and adjoining counties, in the neighborhood of Dungarvin and Warriors Mark, clays in what is designated Cambrian limestone on our old maps. In reality, these clays are associated with what is known as the Gatesburg sandstone. So far as now known these clays are, at least in part, closely associated with the iron-ore pits of that region. They have been studied in some detail by Dr. E. S. Moore for the Pennsylvania Geological Survey and the horizon is well worthy of further examination in other portions of the State where it occurs.

Clays at the Base and Top of the Oriskany Sandstone.—Passing upward in the geological column we come to the base of the Oriskany sandstone—the formation which is so extensively used in Pennsylvania for the manufacture of glass sand. The map (No. 2) represents the extent of the Oriskany in Pennsylvania. This sandstone, while originally deposited as an horizontal formation, has been intensely folded in the process of mountain-making in the State. In general it extends from a point on the Delaware River, a little north of the Delaware Water Gap, in a long and generally narrow belt, southwesterly through Saylorsburg, Kunkletown, Bowmansville, and a little south of Pottsville. It is found then west of the Susquehanna River, south of New Bloomfield, and from there extends in a very irregular exposure to the Maryland state line. Its occurrence is very complicated from the fact that the forming of the mountains brought the Oriskany to the surface in a number of distinct exposures, as is illustrated on the accompanying map (No. 2), there being eleven distinct occurrences of the Oriskany along the Maryland state line. Generally, owing to the character of the Oriskany and the accompanying rocks, it is found in a somewhat vertical exposure. Underlying the Oriskany occurs the Helderberg limestone, and in portions of the State it is separated from the limestone by the thin formation known as the Stormville shales, or the Oriskany shales.

In that portion of the Oriskany exposures extending from the Delaware Water Gap westward through Saylorsburg and Kunkletown to Bowmansville on the Lehigh River, just north of the Le-




Distribution of Oriskany Sandstone in Pennsylvania
Scale of Miles

Map No. 2

high Water Gap, and probably a little west of that point, quite extensive deposits of white clay have been found at the base of the Oriskany. For sometime these clays were thought to have been formed from the decomposition and breaking down of the lower portions of the Oriskany sandstone. Dr. Peck has shown that these clays carry fossils of distinct Helderbergian type, and we must therefore ascribe these clays to the decomposition and breaking down of the Stormville shales, which underlie the Oriskany, and perhaps a phase of the Helderberg limestone. These clays, as has been shown by the mining operations, rest directly upon a sandstone, which the general geology of the region shows is the Shawangunk. The clays at this horizon are being extensively mined at Saylorsburg, and northeast and southwest of that town.

At Shirleysburg, near Orbisonia, in Huntingdon County, a white clay is being mined which is apparently at the *top* of the Oriskany sandstone. This horizon has not been thoroughly examined and nothing is known of the extent or possible occurrence of clays at this horizon, although it is probable that, where the proper conditions exist, clays may be found.

Methods of Mining.

The methods of mining in use vary from place to place. In the neighborhood of Mt. Holly most of the mining is done by drift, which in clays of this character requires quite heavy timbering, and indeed the drifts can be maintained but a relatively short time, as the timbering will not carry the load which is gradually thrust upon it by the slowly creeping clay. At one point, near Mt. Holly, the clay is mined by open cut. The developments near Dillsburg have been made by drifts, while the mining near Narvon is by open cut, there being at that point at the present time an exposure of some eighty feet, with probably forty feet of clay underlying the track level at the present face.

The clays at Warriors Mark and Dungarvin have been mined by open cut, some in the old iron-ore pits, although at places the clay has been directly opened up and is apparently not in contact with the iron ores.

In the region of Saylorsburg the mining is by shaft, and here also

the difficulty of maintaining the workings by timbering is evident. The clay at Shirleysburg is mined by open cut. West of Saylorsburg, near Kunkletown, it is probable that the clay might be mined by open cut.

The proper study of the methods of mining now in use would probably result in changes and lessen the cost of operations. In at least one of the clay mines candles are still used for lighting. At least a portion of the South Mountain area might be mined by open cut, and a thorough study of the methods used would certainly be of advantage to the producers. Apparently not more than 40 per cent of the clay is recovered and the average is probably less than this amount.

Preparation and Uses.

A very considerable portion of the clay now mined is sold in the crude form, no attempt being made to mill it. In general the milling of the clay consists of blunging and screening, with various arrangements of settling troughs and tanks, pressing, drying and pulverizing for the market. Some of the plants use an electrolyte for deflocculation, and acid for again flocculating the clay. In other plants more labor is used than is necessary, due in part to the methods employed. Some plants are not well balanced in their machinery equipment, and were designed apparently without a full knowledge of the behavior of clays and the differences between them and other materials which are ground wet and then concentrated. Without doubt there is room for improvement in the methods of milling in use, and a very marked improvement can probably be made. There does not seem to be a true appreciation of the fact that a very close uniformity of product is necessarily required if the clay is to be marketed as a high-grade material.

The clays as produced are sold both in the raw state and milled. Much of it is used in the steel plants for molding purposes, and some is used in paper manufacture. For the latter purpose it is mainly used as a filler, for most of the clays could not be used for surfacing, which requires a better and more uniform milling to secure a clay which can be used in competition with the imported paper clays.

One of the clays, mixed with ground quartzite or ganister, is used for mortar in the laying of silica brick. Little, if any, is used in pottery bodies. In connection with the possible use of these clays for pottery purposes, it must be said that some appear promising, and it is probable that with better milling they may be used in at least some classes of pottery. These clays carry quite a high per cent of fluxes, and, if so used, provisions must be made for these fluxes in the composition of the batch. Many of the clays carry a high portion of fine silica which should be reduced in amount to allow of their use for ceramic purposes.

Prospecting.

One of the important features in connection with these clays is to know where to look for them. The work done last summer (1918), together with information available from other sources, seems to indicate that it is needless to look for such deposits except at the horizons suggested, and a knowledge of these certainly limits and restricts the areas which are worth investigation. It is useless for us to search for such materials in those portions of the State underlain by heavy horizontal limestones, and it is equally useless to look for good materials where the underlying rocks are heavy, horizontally-bedded sandstones. It would probably also be quite useless in any case to seek such materials where the structure of the rocks, that is, their relation to horizontality, is not suited to the prompt and easy carrying away of the impurities dissolved out in the processes of weathering, as where the rocks have always been practically horizontal. It is for these and associated reasons that the real prospecting for clays is a geological problem.

STATE GEOLOGIST,
TOPOGRAPHIC AND GEOLOGIC COMMISSION OF PENNSYLVANIA,
BEAVER, PA.

COMMUNICATED DISCUSSION.

H. RIES: Dr. Hice's paper calls attention to a series of clay-bearing formations which are of extremely interesting character, *viz.*, the Cambrian and Oriskany. In their unaltered condition they carry little of value, but where the formations carry shales,

schists, clayey limestones or feldspathic sandstones, these are capable of yielding residual clays on weathering, especially, if, as Dr. Hice points out, the beds are tilted so that the surface waters can enter and decompose them.

In Pennsylvania, of course, these residual clays are not in most cases new discoveries, although some of the deposits have been recently opened.

But the point which I desire to emphasize in this connection is that the Oriskany and Cambrian formations which yield these clays in Pennsylvania extend southward along the ranges of the Appalachian province, and that they should be followed, as can be easily done by the use of available geological maps, and prospected for further deposits.

We know that the Cambrian along the west slopes of the Blue Ridge carries a number of white residual clays derived from shales, and the Oriskany has been found to contain white residual clays in West Virginia and northwestern Virginia.

So the search should be continued. As in Pennsylvania, so in the other states where they have been thus far found, the clays are frequently near brown-iron deposits.

Descriptions of many of these deposits will be given in a forthcoming report of the United States Geological Survey.

CORNELL UNIVERSITY,
ITHACA, N. Y.

APPLICATIONS OF THE POLARIZING MICROSCOPE IN CERAMICS.[1]

By Albert B. Peck.

In the rapid advancement and expansion which has characterized industry during recent years and particularly during the stress of the recent war there has been a constant demand for new instruments and devices for research. It has, however, often been easier and more satisfactory to use and develop older instruments along new lines. This is true of the polarizing microscope and, of late, technical practice has turned more and more to it as an aid in solving some of its problems. Sometimes it has been employed alone but very often it has worked hand in hand with the chemist in these tasks with great advantage to both, attaining results which otherwise would have been almost, if not quite, impossible.

While the succeeding pages will deal with ceramic problems, this field is not the only one in which the polarizing microscope is being applied satisfactorily. In a recent article[2] it has been pointed out how the polarizing microscope may be applied to the study of the homogeneity of sugars, salt, flour, photographic developing powders, and chemical preparations and precipitates, thereby detecting adulterants and impurities. In the field of pharmacy excellent results have been obtained recently in applying petrographic methods to the examination of compounds to determine quickly what drugs are present and the purity of other compounds.[3] Perhaps the most recent field into which the polarizing microscope has entered is that of dyes, where its use is contemplated in partially controlling the processes of manufacture of the intermediates and finished products.

[1] By permission of the Director, Bureau of Standards.

[2] F. E. Wright, *J. Am. Chem. Soc.*, **38**, 1647 (1916).

[3] E. T. Wherry, *Ibid.*, **40**, 1063–74, 1852–58 (1918); U. S. Dept. Agr., *Bull.* **679** (1918).

The polarizing microscope[1] is applicable to the study of all minerals or solid substances which will transmit light when in thin fragments and workers in the ceramic field are fortunate in that they make use to such a large extent of inorganic compounds which occur as natural minerals. By the very nature of the development of the polarizing microscope these have received intense study and as a result very complete data concerning their optical properties are available. In the few cases where the compounds encountered in the finished ware cannot be referred to some natural mineral, the very excellent work done by the Geophysical Laboratory in its syntheses often fills the gap. In the organic field, however, the ground has not been so thoroughly covered in the past and this handicap must be overcome in most cases by the production and study of the compounds by each investigator as he proceeds.

When the microscope is spoken of, one immediately thinks of an instrument such as the biological microscope, the chief purpose of which is the examination of minute objects and structures. Such a microscope uses ordinary daylight or artificial light, which is of such a character that its vibrations take place in all directions perpendicular to the direction of propagation. The polarizing microscope possesses all the powers of magnification of the ordinary biological microscope but differs from it essentially in that it makes use of a so-called nicol prism to produce plane polarized light; namely, light vibrating in only one plane. Hence, the name, polarizing microscope.

The earlier polarizing microscopes were used wholly in the study of minerals as they occurred singly or as constituents of the rocks and it is because of this fact that the name mineralogical- or petrographic-microscope is also applied to it. In its early days the observations made with the petrographic microscope were

[1] For complete descriptions of the polarizing microscope and its development, the production of polarized light, and discussions of the various optical properties of minerals in detail, reference may be had to any standard work on petrographic methods such as Idding's "Rock Minerals," Wright's "Methods of Petrographic-Microscopic Research," Johannsen's "Manual of Petrographic Methods," or to F. E. Wright, *J. Am. Chem. Soc.*, **38**, 1647 (1916), or E. T. Wherry, U. S. Dept. Agr., *Bull.* **679** (1918).

almost entirely qualitative in character. It is only in more recent times that it has been used in a quantitative way. While the models of today are essentially similar to the older ones, various improvements in construction have continually been made and accessories added until, in the hands of one trained in its use, it has now developed into an instrument of high precision, both qualitatively and quantitatively.

In carrying out these measurements two methods are in general use. The first is that developed in 1850 by Sorby, an Englishman, the use of thin sections. This method has been the standard method of petrographers and mineralogists. Within recent years another method has been worked out, chiefly through the efforts of the Geophysical Laboratory at Washington in its extensive study of silicate melts. Each has its advantages. The former is most useful in preserving the structure of the body. The latter method, used by the Geophysical Laboratory, is commonly known as that of "immersed grains." The substance is simply crushed to a fine powder, immersed in a liquid of known index of refraction, and the various properties may then be determined on the fragments. It possesses the advantage of allowing the grains to be rolled over and moved around and their optical constants determined in different directions on the same fragment. It furthermore does away with difficulties arising from overlapping grains such as frequently happens in thin sections of fine-grained preparations, giving anomalous results in some cases. The main disadvantage is the loss of structure and texture which sometimes, but not always, results but its advantages seem to outweigh its disadvantages, particularly in fine-grained bodies. European petrographers, however, have not been so quick to adopt it.

Qualitatively, one may study such properties as form, color, cleavage, fracture, vibration directions, and pleochroism. Some of these are self-explanatory but it is not the purpose to discuss them here. Suffice it to say that while they have definite bearing on the study and determination of substances, their importance is not nearly as great as the quantitative measurements.

The four most important quantitative measurements are the index of refraction, double refraction, size of the optic angle, and

extinction directions and angles. Aside from these there are methods of measuring the size of grains in an aggregate and of estimating with fair accuracy the relative proportions in which they are present. The latter, however, has not yet reached the stage where it is as reliable as the other values which may be obtained. Of the quantitative values the index of refraction is by far the most important and the one most often determined. For this reason it may be well to explain how the index of refraction may be determined and used in the study of ceramic materials.

The index of refraction is an expression of the relative velocity with which light travels in air as compared to its velocity in a substance, and by microscopic methods it may be determined with a limit of error of from 0.001 to 0.003 more or less than the true value, under proper conditions and in monochromatic light. In the case of substances such as glass or common salt, belonging to the isotropic group, there is only one index of refraction in all directions but in the anisotropic group to which quartz and feldspar belong, there may be two or three different principal indices of refraction in any one fragment, depending upon what direction the light is traveling through the mineral, and the index for each direction must be determined separately.

The method most used when working with the microscope is that of "immersed grains," previously referred to. A small amount of the finely-crushed material is placed on a microscope slide and immersed in a drop of liquid of known index of refraction,[1] the value of which has been previously determined, and covered with a cover glass. The next step is to adjust the microscope properly so that it allows parallel polarized light to come through and by an iris diaphragm to cut down this light so that only a small amount passes. When we now focus sharply on a fragment we note a bright band of light following the outline of the fragment at its junction with the liquid. This is known as the Becke line effect and by the movement of this bright line as the tube of the microscope is raised or lowered it is possible to tell whether the fragment has a higher or lower index than the

[1] The best practice is to have a set of standardized liquids, ranging from 1.46 to 1.78 or 1.80, which are kept in glass stoppered, covered bottles and differing from each other in index by 0.01 or 0.005.

liquid. For example, suppose the bright line moves into the liquid when the microscope tube is raised. We then know that the liquid is of higher index than the fragment and we take a fresh sample of the powder and immerse it in another liquid of lower index and again note the movement of the Becke line. By using fresh samples of powder and different liquids it is possible to arrive at a point where the fragment is higher than one liquid and lower in index than the liquid next highest in the scale. During this procedure it is also noticed that as the index of the various liquids approaches that of the fragments, the Becke line becomes fainter in intensity and the outline of the fragment tends to merge into the liquid, making it difficult to distinguish the fragment from the liquid. When such a point is arrived at, where the index of the fragment lies between two adjacent liquids in the scale, monochromatic light may be resorted to and the two liquids mixed in various proportions until there is practically no Becke-line effect and the fragment is invisible. The index of the liquid which produces this effect may then be determined on a refractometer and this value then represents the index of refraction of the fragment, with a certain limit of error depending upon conditions which must be judged by the observer.

An alternate method is that of Schroeder van der Kolk. The procedure as far as the preparation of the samples and liquid is the same. Adjustment is made, however, so that converging light is used in place of parallel light and the light is allowed to come through at full intensity. Now when half of the light is shut off by placing the finger or a straight-edged piece of cardboard across the lower end of the condensing system of the microscope, the borders of the fragment appear dark on one side and light on the opposite side. Whether the dark border is toward the shadow of the finger as seen in the field of the microscope or is away from it, determines whether the index of the fragment is higher or lower than the liquid and the observer then knows in what direction to proceed. The change from one method to the other is very easily and quickly accomplished and the two are usually used together; thus one furnishes a check on the other.

A common example of the use of the index of refraction is in the examination of ground feldspar, which is suspected

of having excessive amounts of albite or quartz present because of difficulties from crazing of the glaze. In ground feldspar we commonly find four constituents, orthoclase (potash feldspar) which has indices ranging from 1.519–1.526, microcline (potash feldspar) 1.522–1.529, albite (soda feldspar) 1.532–1.540, and quartz 1.544–1.553. If some of the ground feldspar is immersed in a liquid with an index of refraction of 1.53 and the Becke test applied, we find that the great majority of the fragments have an index slightly less than the liquid, no matter in what direction they may be turned. Many of them show rectangular outlines due to a very excellent cleavage. This indicates that most of the material is orthoclase. Some of the fragments, however, while showing an index less than the liquid in some directions, disappear almost entirely in it in other directions. This indicates microcline. Other fragments which also disappear in the liquid when lying in one direction appear with an index higher than the liquid when turned in another direction. This, then, indicates albite. The fourth constituent shows a higher index than the liquid and also a greater relief or contrast than the albite and this indicates quartz. These facts can also be verified by using liquids of other indices (1.52, 1.54, 1.55) and a check obtained on the previous conclusions. The above procedure can in turn be supplemented by study under crossed nicols, where we find that what was determined as orthoclase shows none or only occasional twinning structures while the microcline shows a very complicated and characteristic fine twinning in which the various sets cross each other at right angles. Albite also shows twinning but it is more simple than that of microcline, while the constituent with the highest index of all (quartz) shows no twinning. Many other phenomena may be used to verify the previous conclusions and with practice one may arrive at some estimate of the relative amounts present and determine whether the albite and quartz are present in amounts exceeding the limit of safety.

The use of a petrographic microscope enables one to gain many advantages. The fineness of the material to be examined will not ordinarily interfere in petrographic work because with the best of modern microscopes practically all the optical properties may be determined on grains as small as 0.01–0.03 millimeter

(1/2500 to 1/1000 inch) in diameter. Some idea of the small size of a grain 0.01 mm. in diameter may be obtained from the fact that such particles when composed of substances like quartz or feldspar, settle as a dust in air at a rate of 25 centimeters per minute and in water at a rate of only 30 centimeters per hour.

Very few branches of science can be said to be really independent of any other and so it is with a petrographic microscope, that while it is often very helpful alone, it is still more valuable when used in connection with the work of the chemist. If the latter wishes to secure pure material, the petrographic microscope enables him to obtain it by detecting impurities and lack of homogeneity. Chemical analysis alone will not enable one to distinguish between a mixture of two substances and a solid solution of the same total chemical composition, except where there is a definite difference in solubilities. With the microscope it is easy to separate the two, since in one case two substances with different optical properties are present and in the other but one substance is seen. Moreover, the optical properties of solid solutions, particularly the indices of refraction, often vary between the limits set by the two end members of the series. This is exhibited by many mineral groups such as the soda-lime feldspars and the olivine group. In the case of feldspars it is possible to determine their chemical compositions with remarkable accuracy by means of the indices of refraction. In Portland cement the amount of free lime or even its presence cannot be detected for a certainty by chemical means alone, while the microscope will readily find this undesirable ingredient by one of several methods.

Another factor which may be of decided advantage at times is the small amount of material with which the petrographer can work when necessary. The average sample of a powder needed at any time when placed on the slide under the objective is hardly larger than a small pin-head and as a general rule not many of these samples are required to obtain the optical properties. Larger amounts at one time make for an undesirable crowding together of the particles in the field of the microscope. It can be seen, then, that the amount of material should cause no disadvantage when only a little is available.

As previously pointed out, the state of the material is not a

matter of great consequence. If it comes to hand in the form of one solid piece, and texture is the principal item of interest, a thin section may be prepared from it. If it is desired to have it in a powdered form, it may be crushed and with the ability to work on grains down to 0.01 mm. in diameter the crushing is not likely to be carried too far.

The saving of time is always an important factor. An instance of the use of the petrographic microscope in this way has recently been given by Dr. F. E. Wright, of the Geophysical Laboratory, in examining some scouring powders.[1] These are usually composed of an abrasive such as ground quartz, flint, feldspar, pumice, or obsidian, and a soap and an alkali such as Na_2CO_3. To make a chemical analysis of such a powder requires considerable time but it is not a difficult matter to distinguish between these three constituents under the microscope. Dr. Wright gave a table showing the relative amounts of each of the main constituents, naming each as quartz, feldspar, etc., soap, or Na_2CO_3, of eight common powders. The whole time consumed was about two hours and the proportions given were of the same order as the longer chemical analysis would subsequently show. No claim is made for absolutely accurate results but the agreement is close enough to give a good indication of their compositions.

The examination of ground feldspar mentioned is another example of how the microscope may be employed to save time. Chemical analysis of feldspar is a matter of days whereas with the microscope a fair idea may be obtained in a comparatively few minutes.

In the following pages some examples from different branches of ceramics will be given in an attempt to show how the petrographic microscope has been used in the past in research to help in the solution of problems. No attempt will be made to include all work along this line nor to give more than brief descriptions of those mentioned. Some are from the writer's own experience while others are taken from widely different sources.

The mineral constitution of Portland cement and the processes taking place in the hydration and setting of it have long created discussion. Many attempts by chemical and microscopic means

[1] *J. Am. Chem. Soc.*, **38**, 1647 (1916).

had been made to determine definitely what compounds existed in the clinker but these were without real success until the Geophysical Laboratory, as a result of their physical-chemical and petrographic studies of melts of mixtures of CaO, Al_2O_3, and SiO_2 ventured the prediction of its constitution. Later work by the Bureau of Standards confirmed this prediction. With the constitution of cement clinker definitely settled, the next step was to prepare the pure components and to determine by microscopic study what products resulted upon the hydration of the cement, what components were affected by the hydration, and what, if any, were inert or affected only very slowly and it was found possible to do these things also. From Portland cement the study has been carried on to other compounds of CaO and Al_2O_3, or CaO, Al_2O_3 and SiO_2, which possess hydraulic and cementing properties. In this study of cement the rate of hydration and the change or growth of the crystalline hydration products have been traced microscopically for long periods in molded specimens of neat and sand briquettes and concrete.

The study of porcelain probably represents one of the oldest attempts to use the polarizing microscope along ceramic lines. Once begun, it has been increasingly used to study the changes which take place during burning, to follow the progress of vitrification and the solution of the clay and quartz. The effect on the microstructure of different temperatures of burning has been studied extensively and also the effect of varying lengths of burn. The relation of the sillimanite which is formed during firing to the quality of the ware has also been the object of investigations. The introduction of small amounts of oxides as additional fluxes has been found to have a very marked effect on the microstructure which is reflected directly in the transparency of the body.

Comparatively little work has been done in the microscopic study of glazes. In the case of non-crystalline glazes its use is mainly to detect impurities such as quartz and albite in the ground feldspar leading to crazing, as was mentioned in the discussion of the index of refraction. In the production of crystalline glazes it is very useful in determining what mineral forms the crystals. The zinc orthosilicate, willemite, is the one most commonly formed, although cristobalite, one of the many crystalline forms

of SiO_2, has also been identified. Manganese silicates and oxides have been partially identified and zinc titanate or titanium dioxide crystals are also thought to have been present in some glazes containing those oxides. This field has been investigated so little, however, that it should present possibilities of excellent results.

While the manufacture of window glass and bottle glass has long been established in this country, that of optical glass has only been developed on a commercial scale since about 1917. One of the first things found necessary was the development of suitable pots for the melting of the ingredients. In this, the microscope had a small share in studying the solution effects of the glass on the pot walls. In the earlier stages of production, before sufficient experience had been gained and schedules standardized, it was found quite profitable to follow the melting process by index of refraction determinations with the microscope. These were found to be sufficiently accurate to enable one to tell when the index was near that of the calculated value for the batch and to be sure that the lead, for example, had been raised from the bottom and thoroughly mixed through the melt in the stirring process. Another important result of microscopic study has been not only the determination of the mineral composition of stones in glass but also it has been shown possible to point to the source of the stones, either batch, pot, crown drops, or devitrification. Having found the cause of the trouble, proper measures may be taken to remedy it.

The microscopic study of refractory brick has shown considerable activity in recent years and the investigations have taken in practically all types, silica brick, magnesite brick, various fire brick, brick made from shale and dolomite, and many types of special refractories. All steps from the raw material through burning to the finished product and even on to the product after it had been in use for some time, have been considered. The microscope offers a convenient means of following the mineralogical changes through different ranges of time and temperature in the firing process.

Silica brick in particular have come in for detailed studies and many facts concerning the changes taking place in firing are now

known. For example, it can be seen that the first changes occur in the fine-grained material which acts as a cement in the green brick. In firing, the original quartz inverts to cristobalite which later reverts to the tridymite form which is more stable at the temperatures at which the brick are ordinarily used. After the fine-grained material, the larger grains of quartz shatter and invert to cristobalite along the cracks and in time may be wholly converted to cristobalite followed by tridymite. It has also been found that brick made from a chert, in place of quartzite as the raw material, will invert more quickly to cristobalite and tridymite—probably due to the finer-grained texture of the chert. Much quartz in the finished brick is undesirable since it renders the brick liable to dangerous expansion in use. A microscopic examination is a quick method of determining whether an excessive amount of quartz is present.

An example of difficulties which an examination of the raw materials may solve is shown by the following case where it was proposed to manufacture silica brick from quartz derived from a large vein running through a granite mass. On preliminary tests of three bricks made out of different samples, two bricks failed entirely, fusing to a glassy mass containing the quartz. Subsequent examination of the raw material showed considerable amounts of feldspar and mica present, caused, no doubt, by the material being taken from points too close to the contact of the vein with the granite.

Other properties such as that of the character of the bonding material of brick may also be studied.

Many other ceramic products, such as spark plugs and electrical porcelains, might be mentioned but the foregoing should be sufficient to indicate the many and varied types of investigations to which the petrographic microscope may be profitably applied. Only a beginning has been made and the future should yield much more.

In the foregoing pages an attempt has been made to convey in a simple manner some idea of the relation of petrographic methods to ceramics. That its importance is being recognized by ceramic manufacturers and others is shown by the fact that they are gradually adding to their research staffs men trained

in this field. The field is almost entirely new and capable of important results in the future.

It must not be inferred, however, that these methods are something which may be absorbed in a short time and then put into practice. Articles appear every now and then which show only too well a lack of thorough training and experience. A thorough training in the fundamentals of the behavior of light in passing through crystalline bodies, backed by experience in the application of these principles to the study of rocks and other crystalline substances, is absolutely necessary and is a matter of considerable time if done rightly.

The demand for petrographers for ceramic work presents several difficulties. In the past the supply of petrographers has been ample because their field was confined almost entirely to mineralogical or geological work. Now, however, with the increased industrial demand, the supply is too limited because it represents a narrow special field which is usually taken up only by graduate students. Due to the attention drawn during the war to the vast importance of the mineral resources of the country, there is no doubt but that many more students will in the future be drawn into the allied fields of mineralogy, geology, and mining and that in this manner many more will work their way into petrography than in the past. It is also true that there are only a few universities properly prepared at present to give courses in the latest methods of using the petrographic microscope, and, furthermore, it unfortunately happens that very few of these universities which are able to offer good training have a ceramic school or offer a few courses in ceramics.

One of the greatest difficulties facing the petrographer who goes into ceramic work is the fact that he immediately finds himself in a field about which he has almost no knowledge. The average petrographer comes with a knowledge of mineralogy, geology and perhaps some physical chemistry but with nothing in the nature of ceramic principles and it is a handicap which requires considerable time to overcome. The obvious remedy for this is the institution in the ceramic schools of the country of courses, in connection with the mineralogy departments, which will give every ceramic student at least a fair understanding of the principles of petrog-

raphy and their application to and importance in ceramics. In this way many no doubt will be led to take up graduate work along the lines of ceramic microscopy.

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COLLOIDAL TRI-CALCIUM ALUMINATE.[1]

By A. J. Phillips.

I. Introduction.

In a previous publication[2] it was stated that tri-calcium aluminate, on mixing with water, hydrated to form an amorphous product which later became crystalline. As the aluminate, together with tri-calcium silicate, is responsible for the changes in Portland cement known as initial and final set, a further study of the amorphous aluminate was made with respect to its behavior with large and small amounts of water and to the alteration in its condition caused by the addition of several salts; in order to obtain some idea as to the way in which the set of a normal cement would be affected under similar conditions.

II. Tri-Calcium Aluminate in True Solution.

1.—**Relation between Various Degrees of Dispersion.**—The material used was that prepared by Bates[3] and consisted almost entirely of $3CaO.Al_2O_3$ with entire lack of crystalline outline; a very small amount of $5CaO.3Al_2O_3$ and traces of $2CaO.SiO_2$ and CaO. Before use it was ignited to remove any water and CO_2 present and sifted through a 200-mesh sieve.

A more or less permanent suspension results in case the aluminate is agitated for some time with a large volume of water and the question arose as to whether we were dealing with a true solution of the aluminate with a mechanical suspension of coarse grains or whether we had present a solid phase which was sufficiently subdivided to be in the colloidal state but which was not sufficiently subdivided to be in the molecular state.

It is generally considered that there is no sharp line of demarcation between coarse suspensions and true solutions, but that there is a gradual progression from coarse to fine suspensions,

[1] By permission of the Director, Bureau of Standards.

[2] Bur. Standards, *Tech. Paper* **43** (1914).

[3] *Ibid.*, **78**, 6 (1917).

to molecularly dispersed, to ionically dispersed solutions. Apparently then we are unable to draw any dividing line in the case of the aluminate and water, as a coarse suspension is readily formed by shaking with water and Klein[1] has shown that definite crystals of hydrated aluminate are formed after a period of time, indicating that possibly the aluminate has gone into solution and when sufficiently concentrated has crystallized out.

Admitting that both molecularly and colloidally dispersed particles enter into the reactions of the aluminate, we examined first that part in true solution.

2. **Solubility of the Aluminate.**—Suspensions of the aluminate in no case gave clear filtrates when single or double filters were used, or even in the case of a filtration through an alundum cone. By continued filtration the filters clogged so that a clear liquid was obtained; but by the time this had occurred the filtration took place at a very slow rate. By dialyzing a suspension through a collodion sack, first tested with a solution of Congo Red to insure the absence of pin holes or leaks, a solution was obtained which reacted faintly for alumina and lime. This was considered sufficient indication that a part of the aluminate goes into true solution.

3. **Hydrolysis.**—Hydrolysis occurs whenever we have the salt of a weak acid or weak base in contact with water. The aluminate being the salt of a weak acid and part of it going into solution, we should expect some hydrolysis; especially since Bates[2] has shown that tri- and di-calcium silicates, both salts of a weak acid and a strong base, split off lime hydrolytically.

In referring further to the literature on cement we find several references to the hydrolysis of the aluminate. Rohland[3] states that the aluminate is hydrolyzed to calcium hydroxide and aluminum hydroxide. If hydrolysis does occur however, we should not expect it to be so complete, but would rather expect the separation of free base ($Ca(OH)_2$) and a residue containing less lime than the original material. This follows from the fact

[1] Bur. Standards, *Tech. Paper* **43**, 15 (1914).
[2] *Ibid.*, **78**, 15 (1917).
[3] *Z. ges. Brauw.*, **29**, 704 (1904).

that if a salt of a strong base and a weak acid is only slightly soluble in water, its solubility will be limited by the solubility of the less basic residue formed by hydrolysis. Again in a case of this kind the increasing concentration of free base in solution will tend to check the hydrolysis; at some point, therefore, we will have an equilibrium established depending on temperature, concentration, etc., between the amount of hydrolyzed and unhydrolyzed salt. Therefore, contrary to Rohland, only in a case such as dialysis in which the free base is constantly being removed could we expect to find the aluminate completely hydrolyzed into free base and free acid. This conclusion of course applies to the silicates and Michaelis[1] states that water never removes all the lime, but a simpler hydrated silicate is formed. Desch[2] states that water hydrolyzes both the silicates and aluminates. Reibling[3] refers to the hydrolysis of the aluminate as one of the factors affecting setting time and Allen and Rodgers,[4] during the preparation of the aluminates of sodium, potassium, calcium and strontium in the wet way, found them to be slightly soluble in water and by it decomposed unless the alkali was kept in excess. As hydrolysis is increased by dilution it follows that it will be decreased as the concentration of aluminate to water is increased.

In a normal cement containing 7 per cent of alumina, the latter will be present entirely as tri-calcium aluminate and therefore 18.5 per cent of the cement will be tri-calcium aluminate. Let us suppose that for a normal consistency paste 23 per cent of water will be required; then for each 100 grams of cement there will be 23 grams of water for 18.5 grams of aluminate. Neglecting the water required to wet the grains of the less rapidly reacting material, there is a little over one part of water for each part of aluminate. From this we should expect that on account of the concentration of the solution there would be little chance of hydrolysis.

4. Ratio of lime to Alumina in Solution.—In order to determine the possibility of hydrolysis some of the aluminate suspensions

[1] *Tonind. Ztg.*, **33**, 1243 (1909).
[2] *Cement*, **12**, 192 (1912).
[3] *Philippine J. Sci.*, (*A*) **6**, 210 (1911).
[4] *Am. Chem. J.*, **24**, 304–18 (1900).

were filtered in a bell jar from which the air had been exhausted, the suspension being dropped from a separatory funnel on to a double filter until the latter had choked sufficiently to give a clear filtrate. The first cloudy portions passing were rejected and the solution passing later was analyzed. In no case did the analyses show the ratio of lime to alumina which is called for by the formula $3CaO.Al_2O_3$ (that is 1.647–1.0), but in every case the lime was lower. There was, however, the possibility of the adsorption of the lime by the filter paper which would tend to reduce the lime ratio.

Of more importance, however, was the fact that the ratios obtained were not constant but varied with time. To test the matter further a cylinder of aluminate and water was molded about a brass tube and dried immediately in a carbon-dioxide-free atmosphere. This cylinder, about $^1/_4''$ thick, 1″ diameter and 3″ high, was placed in a soxhlet extractor; water in a flask below was converted into steam and a condenser above permitted the condensed steam to flow into the extractor until it overflowed. The overflow was not returned to the flask and 100 cc. portions were analyzed at intervals. By running the water in and out slowly, the solution obtained was clear and did not require filtration. The results are tabulated in Table 1.

As may be seen, this experiment furnished no evidence of hydrolysis, for if there was, the free base would be soluble in water and consequently the ratios in solution would show an excess of lime instead of a deficiency.

It is known that the purest water, even conductivity water, contains carbon dioxide so that there is the possibility that a layer of calcium carbonate was formed on the surface of the cylinder, but that the penetration of the carbon dioxide did not follow that of the water. Reibling[1] found that when cement in bins, stored in a stock house, was exposed to moist air containing carbon dioxide, the absorption of the latter was limited to a distance very close to the surface while the water was able to penetrate much deeper. However, this explanation assumes the presence of much more carbon dioxide than we have reason to believe was present. The only other explanation is that furnished

[1] *Philippine J. Sci.*, (A) **5**, 397–8 (1910).

TABLE I.

No.	Al_2O_3, grams.	CaO, grams.	Time.	CaO/Al_2O_3 in soln.
1.....	0.0275	0.0302	3 hrs.	1.096
2.....	0.0489	0.0553	4 hrs.	1.131
3.....	0.0670	0.0782	4 hrs. 23′	1.167
4.....	0.0286	0.1016	5 hrs.	1.230
5.....	0.1221	0.1499	22 hrs. 20′	1.226
6.....	0.1375	0.1682	23 hrs. 20′	1.222
7.....	0.1486	0.1826	24 hrs. 20′	1.230
8.....	0.1563	0.1938	25 hrs. 35′	1.240
9.....	0.2450	0.3255	42 hrs.	1.288
10.....	0.2553	0.3391	47 hrs.	1.328
11.....	0.2620	0.3570	52 hrs. 30′	1.354
12.....	0.3168	0.4356	66 hrs.	1.376
13.....	0.3236	0.4473	69 hrs. 25′	1.382
14.....	0.3293	0.4589	71 hrs. 15′	1.393
15.....	0.3366	0.4730	73 hrs. 40′	1.405
16.....	0.3446	0.4870	96 hrs.	1.415
17.....	0.3453	0.5035	119 hrs. 30′	1.449
18.....	0.3570	0.5196	142 hrs.	1.456
19.....	0.3764	0.5519	166 hrs. 30′	1.465
20.....	0.4068	0.6081	9 days	1.496
21.....	0.4189	0.6260	11 days	1.494
22.....	0.4416	0.6620	14 days	1.500
23.....	0.4588	0.6896	18 days	1.503
24.....	0.4718	0.7096	22 days	1.504
25.....	0.4802	0.7292	28 days	1.519

by absorption; a small amount of calcium ions was absorbed from the solution by the solid aluminate, leaving a solution containing less lime than that required by the formula $3CaO.Al_2O_3$. Thus the presence of an excess of free base in solution is prevented by the aluminate and to this extent hydrolysis is possibly increased by absorption. With regard to the amount of aluminate in true solution, a number of tests were made by shaking aluminate with water in such proportions that a large excess of the solid phase was present and the suspension was then dialyzed. The results obtained in this way were somewhat higher than those in which the suspension was filtered through the filter paper but in no case was there obtained a concentration of more than 0.6 gram per liter

at room temperature. We may therefore conclude that the material in true solution plays a very small part in the hydration of the aluminate.

III. Tri-Calcium Aluminate in Colloidal Suspension.

By shaking the aluminate with water, a small amount, as we have seen, is dispersed through the colloidal state and enters into true solution, the major portion, however, remains as a colloidal solution or suspension.

1. **Dispersion of the Aluminate.**—Bates[1] notes that on mixing the aluminate with water, the grains, whether coarse or fine, agglomerate and hydrate only on the exteriors to a film which is not readily permeable to water; consequently the interiors of the grains will not be hydrated. However, if larger volumes of water are used with continuous agitation, the films may be mechanically removed, permitting access of water to the unhydrated material and resulting in swelling to a volume many times in excess of that of the original volume.

Our suspensions were therefore made by grinding the aluminate with water in an agate mortar to break up the lumps, washing through a small 150-mesh sieve, and diluting to the desired volume in a graduated jar. The jars were then rotated in a shaking machine for periods varying from 5 minutes to 8 hours. These suspensions were then allowed to settle until there was no visible precipitation in 24 hours; the cloudy liquid above the settled material was then drawn off and preserved away from CO_2. One suspension which had been kept for eight months was still cloudy and opalescent, the total concentration of aluminate being about 0.5 gram per liter. We may note in passing that an essential characteristic of the colloidal state is that the substance will exist indefinitely as a suspension of solid (or sometimes liquid) masses of very small size in some liquid medium.[2]

It was noted that if a suspension of aluminate was treated with lime water, or if the suspension was made in lime water, that there was an increase in the amount of aluminate in suspension.

[1] Bur. Standards, *Tech. Paper* **78**, 9 (1917).

[2] Burton, "Physical Properties of Colloidal Solutions," **1916**, p. 9.

There was more swelling and less material settling out in a given period of time.

In a suspension of this character, in which we have present material in true solution as well as that in suspension, the addition of the common Ca ion to the material in true solution would tend to reduce its solubility and cause precipitation. On the other hand, the action of the Ca ions on the suspended material would be explainable on the grounds of adsorption and influence on the electrical charges of the particles, resulting in an increased dispersion. As the effect noted was that of increased dispersion—more material remaining in suspension—it is justifiable to disregard the material in true solution and consider only the colloidal material when we arrive at the effect of added salts to the suspensions. Furthermore, when we consider the action of salts on a normal paste in which the amount of water is greatly reduced as compared with the suspensions, the percentage of soluble material will also be greatly reduced and may be entirely neglected. Therefore, in studying the behavior of the aluminate with either large or small amounts of water with added salts, it is necessary for us to consider only the behavior of the colloidal material.

2. **Method of Dispersion.**—Normally-burned tri-calcium aluminate forms a definite crystal, hexagonal or rectangular in outline, belonging to the isometric system,[1] and we would expect it to follow the behavior of a crystalline salt in going into solution. It does not do this however, as microscopical studies have shown. Zsigmondy[2] makes a distinction between crystals and colloids according to their method of solution. A crystal on dissolving gives its outside layer to the liquid so that at any moment the residual piece has the exact composition of the original crystal. A colloid, though giving up particles to the liquid, also takes up considerable amounts of the medium, a process accompanied by swelling. If the solution process is at any time interrupted, the residual colloid has not the composition of the original material. Crystalline lime behaves in the same manner and this is in part attributed to polymerization of the molecule. It is not a simple molecule but is better represented by the formula (CaO)n. The

[1] Shepherd and Rankin, *J. Ind. Eng. Chem.*, **3**, 225 (1911).

[2] "Chemistry of Colloids," **1917**, pp. 8–9.

crystalline aluminate is also probably highly polymerized and in contact with water acts not as a true crystal but as a colloid, going through a gradual change involving several intermediate steps, until the final result is a hydrated crystalline body.

3. **The Tyndall Effect.**—A suspension of the aluminate was filtered through filter paper until a clear filtrate was obtained, but on placing the solution in a glass cell and passing a beam of light through it, the "Tyndall cone," a characteristic of colloidal solutions, was obtained. A comparison with distilled water in the cell showed only a very faintly defined cone.

4. **Dialysis and Diffusion.**—A suspension of the aluminate, having a total concentration of 0.5 gram per liter, was dialyzed through parchment paper for 24 hours. Coagulation resulted with the formation of a deposit full of cracks resembling those in dried mud. In another case a suspension was made by mechanical agitation in water and was kept in a stable condition for three months, hence it is reasonable to suppose that it would not have suddenly coagulated; but on dialyzing for 24 hours through a collodion membrane it settled out inside the membrane to form cracked plates.

The settling out or coagulation is of course due to the diffusion through the membrane of the Ca ions carrying electrical charges which stabilized the suspension.

The dialyzate in each case reacted slightly for Ca and Al ions but the amount of material was too small for exact analysis.

For the diffusion experiment a sol of aluminate was poured on a 3 per cent solution of gelatine which had been allowed to solidify in a test tube. After 24 hours there was no visible diffusion of the sol into the gelatine. In another case the sol was colored with a little Congo Red solution and again there was no visible diffusion into the gelatine.

5. **Electrical Behavior.**—It is known that a particle suspended in water becomes electrically charged through adsorption of an excess of either positive or negative ions from the solution. The sign of the charge may be determined by dipping the points of two wire electrodes into a drop of the dispersoid on a microscope

slide; or by sending a current through it while it is suspended in a U-tube. For our work an apparatus modeled after the Hardy U-tube, described by Burton,[1] was used, the electrodes being of coiled platinized platinum.

A suspension of the aluminate in water did not migrate at all when distilled water was used around the electrodes, but as soon as the water was made a better conductor by the addition of a trace of sodium chloride, the migration was toward the negative pole. At another time a little of the suspension was filtered and this solution used around the electrodes and in a third case lime water was used. In all cases the direction of migration was toward the negative pole, the particles being positively charged.

There was no visible increase in the rate of migration with the addition of either lime water or solid lime hydrate. This was hardly to be expected since we were dealing with a suspension containing an excess of the solid phase which very slowly settled out. Variations in the concentration of lime water added simply affected the amounts of excess solid phase settling out in a given period of time. That is, increasing the concentration of lime water up to saturation resulted in an increased amount of material being held in suspension without affecting the rate at which it would migrate. For instance:

100 cc. H_2O + 1 g. aluminate, shaken 5 min., settled 8 hrs., gave 4 cc. of sediment, while 100 cc. lime water + 1 g. aluminate, shaken 5 min., settled 8 hrs., gave 1 cc. sediment.

Again, it has been shown that polyvalent ions do not generally increase the amount of the charge on particles of the same sign as themselves.[2]

To recapitulate, the aluminate suspension contains a small amount of material in true solution and a small amount present as a mechanical suspension which separates out on long standing. The major portion, however, has the degree of dispersion required of colloidal dispersions which readily pass through a filter, do not diffuse or dialyze, show the development of the Tyndall cone and are electrically charged.

[1] *Phil. Mag.*, [6] **11**, 436 (1906).

[2] Baudouin, *Compt. rend.*, **138**, 1166 (1904); Gee and Harrison, *Trans. Faraday Soc.*, **6**, 42 (1910).

IV. Suspensoid-Emulsoid Relation.

The absorption of water by the fine particles in suspension leads to a consideration of the nature of the suspension; that is, whether we are dealing with a suspensoid, an emulsoid, or both.

In suspensoids we have a disperse phase which does not combine with the medium to any great extent and if there is combination an emulsoid is formed. Obviously, a disperse phase which takes up a small amount of the medium, or which takes up a large amount through a considerable time interval, will have the properties of both suspensoids and emulsoids. For instance, the metallic hydroxides combine to such an extent with water that they are considered more like emulsoids than suspensoids.

One of the striking properties which the aluminate exhibits is its absorption of water and swelling, by capillary attraction, endosmose and molecular embibing. According to Ostwald,[1] when we say that the disperse phase is composed of exceedingly swollen particles or of particles united to a great number of liquid molecules, we imply that its state is liquid. The emulsoid is then a liquid + liquid system which exhibits more of the properties of the medium than it does of the disperse phase. In addition, emulsoids represent an intermediate state between suspensoids and molecular solutions, not because they have a greater degree of dispersion, but because the liquid + liquid system formed resembles in its physical properties, such as density, surface tension and viscosity, those of the medium more than those of the disperse phase.

An interesting confirmation of the presence of an emulsoid sol is found in the light coagulation of the aluminate suspensions. If allowed to stand in a glass jar near a window, the sides of the containing vessel turned toward the light become speckled with grains of the aluminate which cling there instead of settling to the bottom. There is a time effect connected with this, since it occurs for a short time only after the suspension is made and does not occur at all if the shaking of the suspension is continued for some time before allowing it to settle. These grains are suspensoid particles which have been coagulated by the light rays

[1] "Colloid Chemistry," 1915, p. 51.

and the reason why the phenomenon does not continue is that the material still in suspension is being converted into an emulsoid which is not readily affected by light.

The question as to whether suspensoid or emulsoid is present in greater amount in the suspension is unimportant, since the aluminate + water is an unstable system—the direction of change being an initial combination with water and a final crystallization as a hydrated crystal. The intermediate stages such as suspensoid and emulsoid represent varying combinations with water which themselves are unstable.

The aluminate suspension is not coagulated by heat or by alcohol but is coagulated by freezing. It does not form a gel on evaporation or by dehydration over sulphuric acid, the product in each case being a loose powder. Its properties in general resemble those of the sols formed from the metallic oxides: iron, aluminium and chromium.

V. Relation between Normal-Consistency Pastes and Excess Water.

When we attempt to compare the behavior of the suspensions with that of the normal consistency pastes, which we encounter in troweling the aluminate with small amounts of water or in troweling cement with the amount of water necessary for a normal paste, we meet with difficulties because of the fact that larger amounts of water and more mechanical agitation are used in the preparation of the former. It becomes necessary then to show what differences exist between the two and how far we may go in making comparisons.

1. **Effect of Excess Water.**—In a normal paste the amount of water used will rarely be more than 25 per cent of the weight of the cement, while in a suspension it may be 100 times or more. The amount of water used for the suspensions is more directly comparable with the amount used in observing the behavior of cement with water on a microscope slide. Muth[1] has shown that the closer the water approximates that used in actual practice, the less the amount of crystallization in the early periods, or con-

[1] *Cement Eng. News*, **21**, 14 (1909).

versely, the larger the amount of water the more the crystallization. Again, Klein[1] has shown that specimens of aluminate on a slide begin to develop crystals within a very short time, while a specimen molded with 40 per cent of water is very slightly hydrated within 24 hours, the material being amorphous with no signs of crystallization.

Crystallization, as shown for instance in the character of precipitated barium sulphate,[2] depends on concentration. That is, in very concentrated and in very dilute solutions the precipitate will be in the colloidal state so that it will pass through a filter. With solutions of intermediate concentration there is a decrease in the degree of dispersion of the precipitate which becomes crystalline and does not pass through a filter. This applies to variations in the amount of water used with the aluminate. If a large volume of water is used, a sol is formed consisting of ultramicrons surrounded by films of water having a free path and motion, while if small amounts of water are used, as in the normal pastes, a gel is formed consisting of ultramicrons packed closely together; the only difference being in the amount of associated water.

In the case of an intermediate concentration of water, such as is used on the microscopic slide, the dispersion of the aluminate is decreased and crystals of hydrated aluminate are formed. This crystallization effect resulting from decreased dispersion, which in turn is dependent on the relative concentrations of disperse phase and dispersion medium, has been demonstrated by Bates[3] in the hydration of dicalcium silicate. Here it was shown that the amount of water must be rigidly restricted in order to cause the crystallization of lime hydrate from the disilicate.

2. **Effect of Mechanical Agitation.**—It has already been noted that wetting the aluminate results in the formation of a semipermeable film around the aluminate grains. With mechanical agitation this superficial coating will be broken and allow water to come in contact with fresh surfaces. When we consider the mixing of a sloppy concrete in a mixer, there enters the possi-

[1] Bur. Standards, *Tech. Paper* **43**, 15–17 (1914).

[2] Ostwald, "Theoretical and Applied Colloid Chem.," **1917**, p. 25.

[3] Bur. Standards, *Tech. Paper* **78**, 15 (1917).

bility of the formation of both suspensoid and emulsoid along with the gel. There is sufficient agitation of fine material with water to form a suspension and it follows that there would be no such thing as laitance unless some kind of a suspension were formed.

We then may compare the behavior of the suspensions and normal pastes if we bear in mind that in the suspensions there is a tendency to form a sol while in the pastes the major tendency is toward the formation of an amorphous gel. Microscopical investigations of aluminate and cement pastes[1] have shown that up to 24 hours, which period includes both initial and final set, there is no crystallization but only the formation of amorphous material. Therefore, we may consider that the behavior of the colloidal material in the suspensions is exactly the same as the colloidal material in the normal pastes.

VI. Tri-Calcium Aluminate Gel.

1. **Formation.**—A gel may be formed by a solid taking up the medium or by the coagulation of an emulsoid sol. The degree of dispersion is less than that of a liquid solution and higher than that of the solid from which it was derived. Between these limits the dispersion may assume any value.

In the normal pastes we should suppose that the very fine material would be hydrated and dispersed to a sol which would later coagulate to form a gel with elimination of water, while the coarse material would very slowly hydrate and distend to form a gel.

As a result of ultramicroscopic studies, Zsigmondy[2] states that newly-formed gels are formed of a closely compacted mass of ultramicrons, having structures more or less granular or flocculent, and consisting of a system of islands surrounded by lakes.

2. **The Inherent Water.**—From the rapidity with which a liquid will permeate the entire mass of a gel, it is assumed that the spaces between the ultramicrons are capillary. At the surface of the gel the meniscus of the liquid touching a capillary tube is concave upward and surface tension exerts a pull on the liquid causing it to rise in the capillary. A corresponding and opposite pressure

[1] Klein, Bur. Standards, *Tech. Paper*, **43**, 15–17 (1914).

[2] "Chemistry of Colloids," **1917**, pp. 68–70.

is exerted on the capillary walls, tending to squeeze the ultramicrons together.

Because of the curved meniscus the vapor pressure of the capillary water is greater than the vapor pressure of a plane surface of water.[1] Furthermore, the water associated with the colloid is adsorbed water which is densified and compressed about the ultramicrons. The compression of this adsorbed capillary water results in raising its vapor pressure since as the pressure on a liquid is increased its vapor pressure increases.

Thus in the freshly formed gel we have a pressure exerted on the ultramicrons tending to squeeze them together and also capillary water at a higher vapor pressure than that of normal water; two conditions which have an effect on the relegation or syneresis of the gel.

3. **Syneresis.**—Syneresis consists of the separation of the gel into two phases, a concentrated phase rich in colloid and poor in water and a dilute phase rich in water and poor in colloid; if the gel is left undisturbed for a number of hours and protected against evaporation. The liquid which separates is not pure water but a solution of all the constituents of the gel in both colloid and molecular degree of dispersion.[2] It is the reverse of swelling and postulates the formation and maintenance of the gel for several hours as well as a decrease in the degree of dispersion.

The relegation noted so frequently in connection with the testing of Portland cement is an example of the syneresis of a gel and as noted by Bates[3] is a characteristic of the aluminate. It was found possible to reproduce this phenomenon by stirring 5 grams of aluminate with 5 grams of water in a test tube and slowly adding 5 cc. of 1.21 sp. gr. hydrochloric acid while stirring and cooling the test tube in running water. In a short time the thick paste became solid and if the test tube was inclined and left for 3–4 hours, the syneresis water separated out from the solid residue and slowly solidified to a clear gel which qualitatively showed both alumina and lime. In cases where the tube was not inclined the

[1] Bancroft, *J. Phys. Chem.*, **16**, 395 (1912).

[2] Ostwald, "Theoretical and Applied Colloid Chemistry," **1917**, p. 93.

[3] Bur. Standards, *Tech. Paper* **78**, 10 (1917); *Trans. Am. Ceram. Soc.*, **14**, 558–9 (1914).

gel was always found at the top of the solid residue as though it had been squeezed up. The relegation of cement specimens is more noticeable in th Vicat-ring specimens than in the Gilmore-needle pats, which more nearly fulfills the specification that the gel should be protected against evaporation. The phenomenon has no connection with crystallization but is simply the separation of a watery phase due to pressure exerted within the gel.

In the case of the aluminate gel which is protected against evaporation, the free water will not be lost but the capillary water which has a higher vapor pressure tends to distill out to the surface where its vapor pressure will be normal.

Let us assume that a small amount of this capillary water distills out to the surface, then immediately the radius of curvature of each capillary meniscus will be decreased, surface tension will be increased, the pressure on the ultramicrons will increase, the gel will contract and a further quantity of liquor will be squeezed out. This watery phase does not remain long in contact with the colloid-rich phase, since water is continuously being absorbed by the unhydrated material, so that with time the watery phase is reabsorbed and the mass hardens as a whole.[1]

4. **Coagulation.**—Syneresis is merely one step in the coagulation of a gel and a gradual contraction of the gel takes place continuously. It has been stated that a gel consists of a series of islands surrounded by lakes, such a structure being more or less permeable to water; during the contraction, however, the ultramicrons come into contact with each other, forming a film or cell wall enclosing liquid. That is, we may have the formation of a series of lakes surrounded by islands. Such a structure will be less permeable to water and consequently the loss in water by the gel and further coagulation will be considerably retarded.

As the gel continues to dry out and contract, the effect of increased surface tension becomes noticeable through the tendency of the small particles to assume a spherical shape. This formation of radial spherulites or droplets as a preliminary to crystallization is particularly noticeable with the $5CaO.3Al_2O_3$ under the microscope.[2]

[1] Zsigmondy, "Chemistry of Colloids," **1917,** p. 146.

[2] Klein, Bur. Standards, *Tech. Paper* **43,** 12 (1914).

5. **Variations in Degree of Dispersion of the Gel.**—In concluding this discussion of the formation and coagulation of the gel, we must emphasize the necessity of confining the dispersion within certain limits, in order to control the various physical effects resulting in maximum strength. The hydration to a gel involves the absorption of water, the combination resulting in swelling with a decrease in degree of dispersion. As the amount of hydration is increased, by dispersing the material and offering a greater surface for absorption of water, the material tends to go into solution and the dispersion is increased. We have a constant shifting of the equilibrium, water in colloid $\rightleftarrows$ colloid in water, because of the fact that in hydration most of the water is going into the colloid, and in solution the reverse occurs. Our efforts are confined to getting all the water possible into the aluminate, but owing to variations in the grain size, we cannot do this without getting some of the aluminate into the water.

With regard to the influence of the amount of dispersion on the strength of the hardened material, Bates[1] states that a high percentage of tri-calcium silicate in a cement is undesirable for the development of early strength because of the fact that this material is easily dispersed and remains in a condition in which it readily takes up water in a moist atmosphere and loses it in a dry atmosphere and consequently hardens slowly. It is readily permeable as compared with the aluminate. On the other hand, the aluminate is dispersed with difficulty and is more readily coagulated with the formation of a material having little strength.

6. **Heat Effects.**—On the first addition of water to the aluminate there is an evolution of heat—due to the formation of an exothermic hydrate. This is due to the fact that water is coming into contact with an anhydride. Salts containing all their water of crystallization dissolve in water with absorption of heat and conversely anhydrides dissolve with an evolution of heat. For instance, Thomsen[2] has shown that BaO, CaO and SrO have positive heats of solution, $Ca(OH)_2$ has a very small positive heat of solution, while $(BaOH)_2.8H_2O$ has a negative heat of solution.

[1] Bur. Standards, *Tech. Paper* **78** (1917).
[2] *Ber.*, **16**, 2613 (1883).

The heat evolved by the aluminate will depend upon its previous treatment with regard to exposure to water vapor. That is, the sudden large evolution of heat on mixing the aluminate with water may be lessened or eliminated by causing it to first combine with a small amount of water; by exposing it to moist air, shaking with wet sand, exposure to an atmosphere of steam, etc.[1] In this case, of course, we are dealing not with an anhydride but with a hydrate.

In addition, the solubility of calcium aluminate is greater in cold than in hot water; the absence of a heat effect will therefore favor a greater concentration of aluminate in true solution, thus more rapidly supplying ions to effect dispersion. In aerated cements the absence of a heat effect will likewise favor the solution of calcium sulphate.

It has been shown that in the dissolution of dry colloids there are two heat effects, hydration, an exothermic change, and solution, an endothermic change.[2] Gelatine, gum arabic, gum tragacanth, dextrine, starch, etc., behave like anhydrous salts. Conversely, the aluminate behaves like a dry colloid in evolving heat on hydrating, for the elimination of a heat evolution by preliminary aeration points to the probability that the taking up of water in this case is analogous to the imbibition of water by a dry gel.[3]

In addition to the heat resulting from the formation of a hydrate, there is a disturbance of the equilibrium $(H_2O)_n \rightleftarrows nH_2O$ of the water molecules, which causes an evolution of heat. This is also eliminated when the aluminate is previously aerated because the contact of water with a solid having even the thinnest film of liquid condensed upon it does not give rise to a disturbance of this equilibrium.[4]

If there is sufficient positive-ion concentration to disperse the hydrated aluminate as fast as it is formed, the resultant of the heat effects will be either zero or negative, since the dispersion of the aluminate is accompanied by an absorption of heat. An

[1] Reibling, *Philippine J. Sci.*, (A) **5**, 396 (1910); Candlot, "Ciments et Chaux Hydraulique," p. 349; Bamber, *Concrete* (Concrete-Mill Section), **23**, 23–4 (1916).

[2] Wiedmann and Ludeking, *Ann. Phys. Chem.*, [2] **25**, 145–53 (1885).

[3] Taylor, "Chemistry of Colloids," **1915**, p. 156.

[4] Gaudichon, *Compt. rend.*, **157**, 209 (1913).

explanation of the absorption of heat may be found in a consideration of the Principle of Mobile Equilibrium, a generalization first given by Le Chatelier and Braun.[1] When a factor determining the equilibrium of a system is altered, the system tends to change in such a way as to oppose and partially annul the alteration of the factor. For instance, in the compression of a volume of gas the volume is decreased and according to the principle the system should oppose this volume decrease. It does this by giving rise to an evolution of heat, for the temperature rise tends to make the volume increase. Conversely, if the volume is increased, the temperature will fall.

During the dispersion of the aluminate, involving an increase in volume, or better an increase in surface, the temperature will fall with absorption of heat as this will tend to contract the volume and make it smaller. In the coagulation of the aluminate, which involves a decrease in volume or surface, there is an evolution of heat because the latter tends to oppose the decrease in volume.

VII. Adsorption or Absorption.

The control of hydration is affected to a considerable extent by the adsorption of electrolytic ions. This leads to a consideration of whether we are dealing with adsorption or absorption. When a gas or liquid bathes the surface of a solid, it must either accumulate in a layer on the outer surface or penetrate the latter to a certain degree. In cases where condensation occurs only on the outer surface or in a very thin layer of the surface, the phenomenon is termed adsorption. If there is penetration to the interior it is termed absorption. The essential difference is that in the first case the composition of the material is different on the surface from the rest of the mass while in the second case the composition of the entire mass is changed.

In examining the aluminate we find a good example of adsorption, for the treatment with water changes the composition of the outer surface only, a hydrated film being formed while the interior is unchanged. Any ion activity will therefore be confined to the surface. It is not to be considered that no absorption takes place, for the rupture of the films by mechanical treatment or the swelling

[1] Lewis, "System of Physical Chemistry," **2**, 140–1 (1916).

of the particles will allow the penetration of liquid to the interior. However, under the circumstances with which we are dealing, the first contact of liquid with the solid particles results in the formation of a film and therefore the major effects are surface effects and due to adsorption.

VIII. The Effect of Calcium Hydroxide.

1. **Formation of the Suspension.**—Thus far we have considered the aluminate alone; however, in cements we find the aluminate functioning in the presence of a hydrated-lime solution formed either from the free lime in the cement or from lime split off from the tri-silicate. Therefore we shall consider the effect on the aluminate of a lime-hydrate solution.

It has been previously stated that lime water effects a greater dispersion of the aluminate than does pure water. This is due to the fact that the positive calcium-ions of the lime hydrate are adsorbed by the hydrated aluminate. When the concentration of adsorbed ions becomes sufficiently great, or when a sufficient number of ions have been adsorbed, their charges repulse each other and the aluminate is dispersed. In order to get the repelling action we must suppose that the positive calcium-ions are adsorbed more than the negative hydroxyl-ions. The results show that this occurs or in other words there is a preferential adsorption of one kind of ion.

If we are thus able to demonstrate the formation of a stable sol by adsorption of like charged ions, then in the formation of a sol simply by mechanical dispersion in water something in the nature of a like process must take place. In the case of aluminate and water alone, a small amount is dissolved to form a true solution and from this solution the hydrated aluminate adsorbs ions and is dispersed.

Since water adsorbed by the aluminate grains is densified and compressed by reason of the adsorption, any salts in solution will likewise be compressed and their solubility increased. If the positive calcium-ions are adsorbed, the negative hydroxyl-ions are left in higher concentration around the grains than in the rest of the solution. They will therefore tend to diffuse away into the surrounding liquid in order to equalize the concentration.

2. **Coagulation of a Suspension.**—The aluminate has a limited capacity for the adsorption of positive ions, so if the concentration of negative ions is sufficiently increased, at some concentration of the latter, the positive charges on the aluminate will be neutralized by the adsorption of the negative ions because of their increased concentration. This will result in the precipitation of the uncharged aluminate, however, as the charge is neutralized and the material coagulates; the adsorbing surface is decreased and consequently the ions which were held by adsorption are given back to the solution to exert a dispersive effect on undispersed material. For this reason the dispersive effect will constantly be working against the coagulating effect, which explains why the concentration of negative ions must be so increased. The process being a reversible one, we may express it by the following reactions:

$$\boxed{CaAl} + Ca(OH)_2 = \boxed{CaAl}\,Ca(OH)_2$$

$$\boxed{CaAl}\,Ca(OH)_2 \rightleftarrows \boxed{CaAl}\,Ca + 2\overline{OH}, \quad \text{where } \boxed{CaAl}$$

represents an ultramicron of calcium aluminate without regard to size, form or composition.

In order to obtain a precipitating effect with lime hydrate, the concentration must be very greatly increased because of its slight solubility in water. A much weaker solution of sodium hydroxide may be used to show the precipitating effect largely because in this last case we have to overcome the stabilizing effect of a monovalent cation while in the former case we are dealing with a divalent cation.

3. **Effect on the Normal Pastes.**—It is of interest to note the behavior of hydrated lime with the aluminate and the restricted amount of water required for normal-consistency pastes. We should expect it to exert a dispersing action in small amounts; however, it had no effect in preventing a flash set from taking place, but on working the paste for several minutes to overcome the granulation, a considerable retardation in the time of set was noted. This is, of course, similar to the flash set observed when unplastered cements are treated with water.

A pat of aluminate with 80 per cent of water became hard enough to support the Gilmore needle in four hours, while by

substituting lime water for distilled water, initial set was not attained in forty-eight hours. By increasing the percentage of hydrate very considerably the setting time was diminished as follows:

5 g. aluminate —4.0 cc. H_2O	Set in 4 hrs.
5 g. aluminate —0.05 g. $Ca(OH)_2$ —4 cc. H_2O	Set in 27 hrs.
5 g. aluminate —4.0 g. $Ca(OH)_2$ —7 cc. H_2O	Set in 1 hr. —40 min.

This illustrates the effect of increasing the total ion concentration over and above the limit of the adsorptive capacity of the aluminate for positive ions.

The tests, while not comparable with the larger amounts of cement and water used for normal pastes as regards period of working, radiation of heat, etc., are comparable among themselves and suffice to show a difference between the presence of large and small amounts of hydrated lime.

Spackman[1] has noted that the effect of mixing 90 per cent of hydrated lime with 10 per cent of aluminate is to increase the rapidity of hardening. He states in addition that it causes the lime to become colloidal or form solutions in which the lime is suspended. This is, of course, an indication that the aluminate adsorbs the lime and is dispersed. It may also be noted that neither hydrated lime nor burned lime form permanent suspensions in water. In fact, they settled so rapidly that we were unable to determine whether the material migrated under the influence of the electric current.

We find references all through cement literature to the effect of lime in causing hydraulic qualities to be developed. For instance, Michaelis,[2] in considering the hardening of cement, states that when a sufficient concentration of lime hydrate is reached, a gel is formed. This, as we have explained, is the concentration of positive ions necessary to cause dispersion. Again Zulkowsky[3] states that barium, strontium, calcium, sodium and potassium oxides bring out the hydraulic properties of blast furnace slag. The significant statement is made that "very basic slags need no alkali addition," due to the fact that a part of the material goes

[1] *Proc. Am. Soc. Testing Materials*, **10**, 318 (1910).

[2] *Tonind. Ztg.*, **33**, 1243 (1909).

[3] *Ibid.*, **22**, 285, 316, 363 (1898).

into true solution, ionizes, and furnishes sufficient concentration of ions to disperse the material.

Further, the statement is made that these alkali additions do not combine, for they may be washed out from the hardened cement. This is an indication, as has already been pointed out, that ions are adsorbed by the immense surface furnished during dispersion, but as soon as the surface is decreased by coagulation, the adsorbed ions are released and may be readily removed.

Finally, there are numerous patented processes involving the treatment of molten slag with solutions of the alkali and alkaline earth salts, as well as salts of iron, aluminium and chromium, for the purpose of securing a hydraulic material. The multiplicity of salts used can only be explained through the adsorption of ions of the same kind of electrical charge, their mutual repulsion causing dispersion and the further adsorption of oppositely charged ions to neutralize the previously adsorbed ions thus causing coagulation.

IX. The Effect of Calcium Sulphate.

1. **Effect on the Suspension.**—In shaking the aluminate with water and varying percentages of plaster, from one to twenty per cent, a very slight increase in the rate of migration was noted. It was almost inappreciable and experiments along this line were discontinued as in all cases the suspension remained positively charged.

With increasing amounts of plaster, other conditions remaining constant, there was a greater amount of sediment settling out in a given period of time. With no plaster, a fine-grained sediment was secured which was difficult to filter and which clung tenaceously to the filter paper. As the amount of plaster was increased, the precipitated material became more flocculent, the size of the flakes settling out became larger, and filtration became easier. This was especially noticeable with 10–15 per cent of plaster. With smaller amounts the material settled out, leaving a cloudy, opalescent liquid above but with over 10 per cent the supernatant liquid clear and transparent. The character of the sediment also changed, as with small amounts of plaster the precipitate settled out in a hard mass which was removed only by scraping the bottom of the glass jar with a rod, while as the plaster was in-

creased the sediment became softer and could be poured out along with the liquid.

2. **Adsorption of the Sulphate Ion.**—At no time did the filtrates from the suspensions give a reaction for sulphate even in cases where as much as 20 per cent of plaster was used. This phenomenon in connection with cements has been noted by a number of investigators. Bates[1] notes that the plaster in cements is held in a form which prevents its removal by distilled water and further in the treatment of cements or aluminate with sulphate solutions that very much more is fixed or adsorbed than is necessary for the formation of tri-calcium sulpho-aluminate. Candlot[2] states that if cements are shaken with water and the latter drawn off and analyzed, there is a decrease in the amount of sulphate present up to the time of set, when there is none present. Also Deval[3] notes that hydrated cements seem to retain sulphate which cannot be washed out with water.

3. **Retrograde Adsorption.**—If an adsorbing surface change through agglomeration, crystallization, etc., its adsorptive power will change and the adsorbed salt will be less firmly held.[4] This action, which is called retrograde adsorption, has been demonstrated by Hase[5] in regard to the adsorption of methylene blue by colloidal sulphur, the blue being returned to the solution as the sulphur changes its degree of dispersion. Again Wagner[6] has shown that in the hydrolysis of the salts of aluminium, iron, etc., the liberated acid is first adsorbed by the dispersed material, but as the particles increase in size, the adsorption is diminished and the liberated acid is returned to the solution.

We were concerned with this retrograde adsorption on account of the gypsum crystals noted in hardened cements. Apparently either the sulphate has been incompletely combined with the aluminate during mixing and crystallizes at some later time, or else when the aluminate crystallizes with decrease in its degree

[1] Bur. Standards, *Tech. Paper* **12**, 36–7 (1912).
[2] "Ciments et Chaux Hydraulique," p. 323.
[3] *Bull. soc. encour. ind. nat.*, **101**, 96 (1901).
[4] Bancroft, *J. Phys. Chem.*, **18**, 549 (1914).
[5] *Kolloid-Z.*, **17**, 153 (1913).
[6] *Monatsh.*, **34**, 95 (1931).

of dispersion the adsorbed sulphate is given up and eventually crystallizes.

To test the matter, a number of samples of aluminate with 10 per cent of plaster and a large excess of water were shaken for one day, allowed to settle for varying periods of time, and the filtrates from these suspensions analyzed for sulphate. The periods selected were 1, 3, 7, 14 and 28 days and in no case was a positive reaction for the sulphate ion secured although the aluminate had visibly agglomerated. Thinking that possibly the amount of water used had not been favorable to the crystallization of the aluminate, a sample which had been treated as above and the suspension allowed to stand for four months, was slowly evaporated over sulphuric acid in a vacuum desiccator. The evaporation to apparent dryness required one week's time and the water solution was examined at intervals for the presence of sulphate. As none appeared in solution, the moist residue was shaken with water and a small amount filtered off. As no sulphate was found here, the residual material was dialyzed and in the dialyzate a satisfactory reaction for sulphate was secured.

As we shall later show, the aluminate is able to adsorb undissociated salts from solution. The adsorption of undissociated calcium sulphate, which may hydrate in place and later crystallize, eliminates the possibility of determining whether or not the sulphate has been completely or incompletely incorporated with the aluminate during mixing.

4. **Coagulation.**—It is known that increasing amounts of plaster or gypsum affect the coagulation or setting time of cements in various ways. For instance, Reibling[1] states that as the percentage of plaster is increased, the set takes place earlier, later, and then earlier. No adequate explanation of the cause of these changes has ever been given but we shall attempt to show that they may be readily explained by a consideration of the colloidal state of the aluminate.

For testing the rate of coagulation, pats were made consisting of aluminate, water, gypsum or plaster and hydrated lime. The water at 20° C in all cases was equal to 50 per cent of the weight

[1] *Philippine J. Sci.*, (*A*) **6**, 226 (1911).

of aluminate and the hydrated lime equal to 2 per cent of the same. The mixing period was limited to exactly one minute and the percentage of sulphate added was plotted against the setting time as shown in Fig. 1.

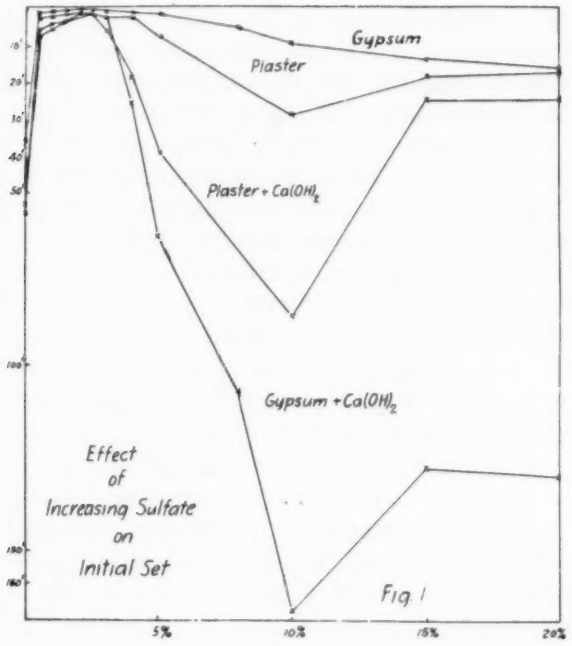

FIG. 1.

4*a*. **The First Acceleration.**—If the aluminate is mixed with water an exothermic hydrate is formed, heat is evolved, and coagulation follows the evolution of heat. However, if the pat is troweled following the flash set, the coagulated hydrated film is broken, positive ions are adsorbed from the aluminate in solution, and the hydrated aluminate is dispersed. The setting time or coagulation then takes place at a later period. In the case of the pats to which no hydrated lime was added, the initial set was retarded to 38 minutes as compared to 53 minutes with those pats in which 2 per cent of hydrated lime was present.

With the addition of plaster in small amounts, the change in

viscosity which allows the pat to support the needle indicating initial set, takes place sooner. The time of set is accelerated to a minimum so that coagulation and evolution of heat takes place while the material is still being mixed. There is this difference, however, from the pats containing no sulphate, in that the latter, while setting at once were reworked and the set delayed, but in the case of those containing up to 3 per cent of sulphate, they remained a crumbly, loose powder even with continued working and could not be formed into a pat.

The setting time in every case is a resultant from the forces tending to disperse the material and those working toward coagulation. Up to 3 per cent plaster or gypsum, with or without hydrated lime, the coagulating forces are in the ascendency and are so powerful as to prevent dispersion of the material by reworking to break up the coagulated film.

Dehydration Effects.—With amounts of plaster or gypsum up to 3 per cent, the set took place in 1–2 minutes. As there was not sufficient elapsed time for the sulphate to go into solution and crystallize out as the di-hydrate, we may eliminate this effect at once. There remains then the probability of a dehydration; a part of the water associated with the aluminate was requisitioned by the sulphate which is able to combine it to form a chemical hydrate—the amount of water necessary to take all of the sulphate into solution being in excess of the total water furnished for both aluminate and sulphate.

We assume that there is a dehydration of the aluminate for the following reasons: Though ions and molecules are admitted to hydrate in solution, it is not conceded that the water in less dispersed material is stoichiometrically combined. In this latter case it is considered that the water molecules are simply gathered more closely around and compressed about the particles.[1] The fact that the water in gels may be replaced by carbon disulphide, ether, alcohol, etc., without any great change in the character of the gel, points to the fact that the water is not chemically combined but is present as adsorbed water filling the spaces between the ultramicrons.[2]

[1] Tyrer, *J. Chem. Soc.*, **99**, 871 (1911).

[2] Zsigmondy, "Chemistry of Colloids," **1917**, p. 139–40.

The water in the colloidal aluminate formed in the early stages of hydration is therefore not chemically combined but merely associated water; there is little or no affinity between the two while the water in the gypsum is chemically combined, indicating considerable affinity. According to Cavizzi,[1] calcium sulphate in solution forms a stable hydrate containing much more than 2 H_2O.

Although there is not sufficient water present to take all of the sulphate into solution and form any such hydrate, the affinity for water exists and the sulphate will strive to secure the necessary water. The partition of water between the aluminate and sulphate will be but slightly affected by the relative proportions of the two, but will be largely influenced by the chemical affinity of the latter for water, an affinity which is lacking in the colloidal aluminate.

The dehydration of a heavily hydrated material involves at first an increase in the degree of dispersion, the swollen particles become smaller due to removal of associated water. If dehydration is continued, as in the case of an evaporation to dryness, the increased dispersion is followed by a decreased dispersion. There is an agglomeration of the particles with decrease in the total surface. The aluminate is not heavily hydrated in two minutes' time, so that the chief effect of the plaster will be a dehydration resulting in agglomeration of the particles with a decrease in dispersion. This is what occurs in "flash set." The effect is not due to the fact that plaster is partially dehydrated as compared with gypsum, for the latter in amounts up to 4 per cent has the same effect.

Rohland[2] has called attention to the acceleration of the initial set of cements by the addition of small amounts of calcium and aluminium sulphates. It will be noted that both of these salts crystallize with water of crystallization and it has been found that the larger the amount of solvent combined as solvent of crystallization, the larger is the amount held in combination as a hydrate when in solution.[3] This of course postulates a desire or affinity

[1] *Gazz. chim. ital.*, [1] **44**, 448 (1903).

[2] *Kolloid-Z.*, **8**, 251 (1906).

[3] Jones and Getman, *Am. Chem. J.*, **31**, 303 (1904).

on the part of the salt for water even though it is not in solution.

4*b*. **The First Retardation.**—In the addition of the above salts in small quantities the chief effect noted is that resulting from the desire to associate a large number of water molecules with themselves. When we add more than 4 per cent of plaster or gypsum under the conditions noted, we begin to see the effect of the ion dispersion already noted under the treatment of the aluminate with hydrated lime; in that the plasticity of the paste is increased and the heat evolved is less. The presence and adsorption of an increased number of positive ions gradually overcomes the coagulative effect caused by dehydration, the resultant being a retardation of the speed of coagulation.

The introduction of 2 per cent of hydrated lime along with the plaster or gypsum has a marked effect in still further retarding initial set. This is because we have added a divalent cation with a monovalent anion and the concentration of the latter must be considerably increased before its negative charge will neutralize the first adsorbed positive ions. It is obvious that 5 per cent of hydrate with 5 per cent of plaster will be more effective in retarding the set than will 10 per cent of plaster, although the same number of positive calcium ions will be present in each case. The curves for the changes in setting time with increasing concentrations of plaster and gypsum are shown in Fig. 1.

Rate of Addition and Solution of Retarder.—Two factors enter into the dispersion of the aluminate by the addition of positive ions—the concentration of the ions and the rate at which this concentration is attained. It has been found that the coagulation of a sol depends not only on the concentration of the added salt but also upon the rate at which it is added.[1] For instance, arsenic sulphide sols are much more indifferent to a slow addition of barium chloride than to a sudden addition. The same condition applies to the dispersion of the aluminate, in that the latter will absorb water and flocculate, but if there is an electrolyte dissolved in the water, it will adsorb a more or less concentrated solution of electrolyte and thus reduce the proportion of adsorbed water. The same result is attained if the aluminate is agitated

[1] Burton, "Phys. Properties of Colloidal Solutions," **1916**, pp. 148–9.

with a sufficient amount of water for some time, in that some of the aluminate goes into true solution and thus furnishes an electrolyte in contact with the undissolved material. Furthermore, if the positive-ion concentration in solution is high enough a dispersive (deflocculating) effect is secured in opposition to the coagulation which is secured by the use of pure water. Thus the rate at which the positive ions go into solution as in the case of a difficultly soluble salt and the rate at which the necessary concentration of these ions are brought up to the aluminate are the two chief factors in causing a retardation of the set.

In comparing plaster and gypsum, the former dissolves faster and it would seem reasonable to suppose that 5 per cent of plaster would be more efficient than 5 per cent of gypsum in effecting dispersion. This was found to be true, the plaster retarding the set to 9 minutes while the material containing gypsum set in 2 minutes. It must be borne in mind, however, that we did not allow for the water in the gypsum but simply added 5 per cent of the weight of the aluminate in either case. A comparison of the actual SO_3 content of each would tend to bring the results closer together.

4*c*. **The Second Acceleration.**—As the concentration of plaster is increased beyond 10 per cent, the neutralizing action of the negative ions is exerted and the setting time tends to be accelerated. In addition an acceleration caused by the setting of the plaster itself becomes distinctly noticeable.[1] This acceleration does not occur to such an extent with gypsum and the rise in the curve with hydrate is partially due to the fact that the water added was kept constant in all the specimens and as the amount of retarder was increased the ratio of water decreased.

4*d*. **The Second Retardation.** *Salt Peptization.*—As the amounts of plaster or gypsum are increased over 15 per cent the initial set is again retarded and the final set, which had previously immediately followed initial set, is also delayed, the interval in some cases being as high as fifty minutes. That we have a retardation is evidenced by the shape of the curve, which should

[1] Meade, "Portland Cement," 1903, p. 309; Reibling, *Philippine J. Sci.*, (A) 6, 229 (1911).

follow a straight line if we consider that as increasing amounts of plaster are added the set should be correspondingly decreased, the setting time tending to approach that of plaster alone.

This retardation is due to the adsorption of un-ionized salt. We are dealing with an un-ionized salt in these cases because the concentration is too great to allow of any considerable dissociation taking place. We encounter then the effect resulting from the adsorption of both ions of the salt which results in a kind of dispersion known as salt peptization.

We start with an ion peptization because one ion is adsorbed more than the other; with increasing salt concentration the adsorption of the first ion (Ca) varies but slightly with the concentration while the adsorption of the second ion (SO_4) continues to increase relative to the first, until we get neutralization of the first and coagulation. At the same time the adsorbed salt is tending to peptize the material so that with still greater salt concentration we should expect salt peptization to overcome coagulation. The possibility of peptization by an adsorbed salt is generally overlooked because an increase in concentration of peptizing salt is apt to cause coagulation.[1]

The slowing up of both initial and final set thus results from the adsorption of increasing amounts of sulphate, the peptizing effect resulting from this adsorption acting in opposition to the coagulating effect. The effect of this adsorption is especially noticeable in the suspensions of aluminate in water. With increasing amounts of plaster, coagulation was effected in every case but a soft, mushy precipitate was obtained, constantly increasing in volume as the sulphate was increased. Bates[2] calls attention to the fact that the addition of increasing amounts of sulphate to cements has a tendency to make the initial set quicker and the final set slower. This salt peptization is not confined to calcium sulphate, as it has been shown that a number of compounds such as tannin, straw infusion, oxalic acid, quinoline, etc. all exert a retarding effect on the final set of cements.[3] The effect here is not due to a high concentration preventing dissociation

[1] Bancroft, *J. Phys. Chem.*, **20**, 102–3 (1916).

[2] *Proc. Am. Soc. Testing Materials*, [11] **15**, 126 (1915).

[3] Benson, Newhall and Tremper, *J. Ind. Eng. Chem.*, **6**, 795 (1914).

but to the fact that at any concentration these salts are but very slightly dissociated.

Heat Effects.—With the normal pastes in which plaster or gypsum was used without any lime hydrate, at the lower concentrations there was a noticeable evolution of heat before the material set. With 2–4 per cent of plaster a smooth paste could not be obtained, but when 2 per cent of hydrate was added, a plastic paste was obtained with all concentrations of sulphate—the heat developing just before or at the time of set. It should be noted that 2 per cent of hydrate is sometimes added to cements containing 18–20 per cent of aluminate; the addition of 2 per cent of hydrate to 100 per cent of aluminate in our case represents a much smaller ratio and at the same time it was very effective. In the same way an addition of 20 per cent of plaster to 100 per cent of aluminate represents an addition of about only 4 per cent to a normal cement.

With amounts of plaster and gypsum exceeding 10 per cent the heat evolution was distinctly noticeable about three minutes after initial set had taken place, showing that the heat evolved was the result and not the cause of coagulation of the gel. This, as has been shown, is due to an effort on the part of the system to resist a contraction in volume.

In view of the erratic heat effects noted above in connection with the coagulation of the gel it seems unlikely that there is any connection between a maximum evolution of heat and the time of initial set. Various experimenters have determined the heat rise for cements but with one exception the presence of interfering elements has prevented their curves from assuming any one general shape.[1] In a normally-setting cement there may be a rise due to hydration which is compensated by an adsorption of heat accompanying dispersion. In cases where the final set is delayed, the heat of coagulation is slowly disseminated and no great rise is noted, whereas, in the case of a quick coagulation the positive heat effect will be much greater than any of the effects hitherto

[1] Taylor, "Practical Cement Testing," p. 92; Gary, *Concrete Constr. Eng.*, **1906**, p. 1,350; Hossbach, *Tonind Ztg.*, **33**, 1083 (1909); Watertown Arsenal Reports, **1901**, p. 493; Cushman, *J. Ind. Eng. Chem.*, **4**, 728–30 (1912).

noted. In the case of a continuous agitation of the cement paste, as proposed by Beals,[1] who secured curves of the same general shape, the continued agitation of the cement will cause an increase in the adsorption of heat due to increased and continued dispersion. The rise in the curve indicating coagulation will therefore not correspond with the initial set of a normal paste because of the continued dispersion which is effected.

The Fineness of the Plaster.—The plaster used to secure the curves shown in Fig. 1 was that portion passing a 300-mesh sieve and, in cases where gypsum was used, it was ground under alcohol, passed wet through a sieve, dried at 50° C, and sifted through a 300-mesh sieve by tapping. A microscopical examination of the powder showed it to have the same refractive index as gypsum.

Rohland[2] notes, concerning the addition of retarders, that in general with equal additions, dissolved substances will have a stronger effect than solid difficultly-soluble materials. So that the finer the retarder is ground, in the case of plaster, the nearer will it approach the properties of a liquid. In adding calcium sulphate to cement in order to retard the set, it is customary to add it while crushing the clinker in the ball mills; its progress, then, through the clinker tube mills (or their equivalent) will result in its being ground very fine as it is softer than the clinker. To make up for this dispersion of the sulphate during grinding, we pulverized the material separately.

The results shown in Fig. 1 are open to criticism on account of the fact that the water was not varied as the percentage of solid material was increased—which would cause set to take place sooner than otherwise. In order to show that increased adsorption follows as the retarding salt is increased in fineness, a large sample of plaster was sifted through a nest of sieves and the material remaining on each sieve was used with aluminate in each case. A constant quantity of water, plaster and aluminate was used; 10 per cent of plaster, 50 per cent of water and 2 per cent of hydrate in cases where the latter was employed. The only variable was the grain size of the plaster.

The results are shown in Fig. 2 in which the setting time in

[1] *Concrete-Cement Age*, **3**, 45–6, 52–9 (1914).

[2] "Der Portland Zement," **1903**, p. 13.

minutes is plotted against the fineness of plaster. The effect of the addition of hydrated lime is particularly noticeable with the plaster retained on the 240-mesh sieve. Without hydrate the set is delayed to a maximum and with finer plaster its own set begins to affect the setting time of the material. With the addition of 2 per cent of hydrate, the dispersion of the aluminate is much increased and this dispersive action prevails to a greater extent over the coagulative forces.

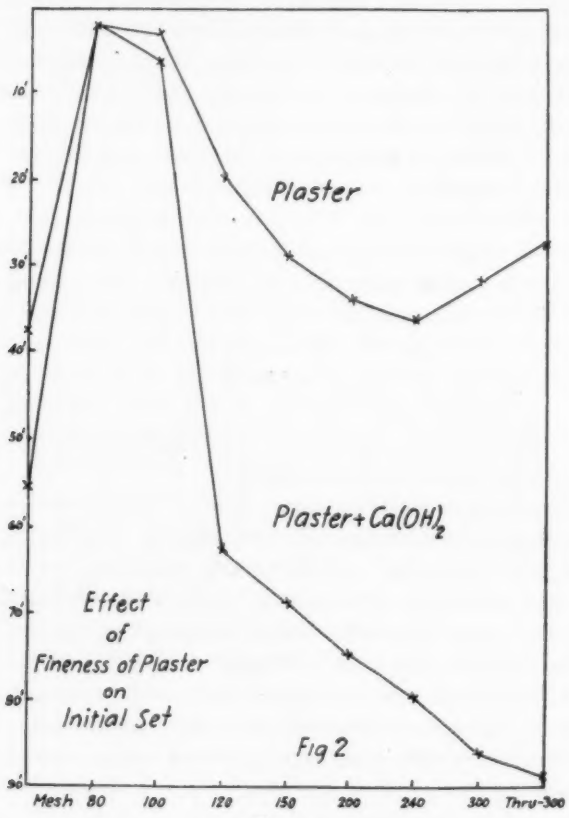

FIG. 2.

The Character of the Pats.—The pats resulting from the tests of the aluminate, as shown in Fig. 1, were in some instances

placed in cold water immediately after initial set and in other cases were kept 24 hours before immersion. As they were not visibly affected after one week's immersion, they were given the customary five hours' bath in steam and in no case did they become soft and mushy. With plaster or gypsum under 10 per cent there was a development of fine cracks which was especially marked in the samples containing only 2–3 per cent of retarder, but those having over 10 per cent were sound and hard. In some cases the surface was chalky but underneath this surface-layer the pat was hard and not readily scratched.

Those pats remaining from the tests, shown in Fig. 2, were sound in cold water but after a time developed radial cracks which were especially noticeable in the coarse plaster samples. A microscopic examination of the hardened pats showed that in every case gypsum crystals were present. In those containing the coarse plaster, the aluminate grains showed dark centers of unhydrated material, a ring of hydrated material, and the gypsum crystals arranged around the outside of this ring. As the plaster increased in fineness, the unhydrated material grew less and the gypsum crystals were scattered through the gel instead of being ranged around the outside. The increased fineness of the plaster therefore resulted in increased adsorption by and better dispersion of the aluminate.

X. Summary.

1. Tri-calcium aluminate, with a large excess of water, forms a suspension containing small amounts of coarsely dispersed and molecularly dispersed material, the major portion being dispersed to a degree comparable to those colloidal suspensions which readily pass through a filter, do not diffuse or dialyze, show the development of the Tyndall cone and are positively charged.

2. The colloidal aluminate is not coagulated by heat, is coagulated by freezing, has a large capacity for the adsorption of ions and undissociated salts and its properties in general resemble those of the sols formed from the metallic oxides Fe_2O_3, Al_2O_3 and Cr_2O_3.

3. With the restricted amounts of water used in cement pastes, the aluminate is converted into and remains as a gel, at least during the first 24 hours after mixing.

4. The rate of dispersion of tri-calcium aluminate to the gel state is influenced by its previous exposure to moisture, the amount of heat developed during hydration, the adsorption of positive ions, the valency of the ions and the amount of dissociation of the salts furnishing these ions.

5. The rate of coagulation is affected by the amount of dispersion effected, the syneresis of the gel, the neutralization of previously-adsorbed positive ions by negative ions, the adsorption of undissociated salt and with the addition of plaster, by the fineness and set of the plaster itself.

XI. Acknowledgments.

It is a pleasure to state that this problem was suggested by and the work carried out under the direction of Mr. P. H. Bates of the U. S. Bureau of Standards, to whom acknowledgment is hereby made. We are also indebted to Mr. A. B. Peck for the examination microscopically of a number of specimens and to Mr. J. C. Evans for assistance in the analytical work.

PHILADELPHIA, PA.

THE INFLUENCE OF TEMPERATURE ON THE TRANSMISSION-FACTOR OF COLORED GLASSES.

By M. Luckiesh.

There are numerous gaps in our knowledge of the physics and chemistry of colored glasses which either have not been spanned at all or have been flimsily bridged by theory supported by inadequate experimental data. It appears to the writer that physical investigations of many of the phenomena pertaining to colored glasses are likely to be most fruitful sources of information, especially if these are carried out in parallel with chemical investigations. It is not the purpose of this brief note to discuss the field in general but to present one of the many interesting phenomena pertaining to colored glass which doubtless will be explained eventually through physical investigations.[1] Hyde, Cady, and Forsythe,[2] in studying red pyrometer-glasses, noted the influence of temperature on the transmission characteristic of a red glass and investigated this influence for temperatures from 20° to 80° C. The transmission-factor of the red glass was found to be appreciably less for various wave-lengths at the higher temperatures than at the lower temperatures.

It appeared of interest to ascertain how generally the transmission-factors of colored glasses were affected by temperature. In a preliminary study it did not appear worth while to investigate this question spectrophotometrically,[3] therefore only the transmission-factor for total visible radiation was considered. However, an idea of the change in spectral transmission is gained through the change in color of the specimen as its temperature is altered. It is hoped that at a later date a careful study of this

[1] M. Luckiesh, "The Physical Basis of Color Technology," *J. Frank. Inst.*, **184**, 227 (1917).

[2] Hyde, Cady and Forsythe, "Effective Wave-Length of Transmission of Red Pyrometer Glasses," *Astrophys. J.*, **42**, 302 (1915).

[3] M. Luckiesh, "Color and Its Applications," **1915**, D. Van Nostrand Co., New York.

phenomenon can be made spectrophotometrically and in parallel with chemical investigations.

In order to eliminate the annoyance of large color-differences in determining the transmission-factors at different temperatures, a given specimen was cut into two pieces and one was kept at a temperature of 30° C, while the temperature of the other was altered gradually from this temperature to 350° C. The transmission-factor of a colored glass, of course, varies with the illuminant so that such a value is indefinite unless the illuminant is specified. In this preliminary account it appears sufficient to state that the illuminants used were gas-filled Mazda lamps operating at normal voltage. A continuous check on the constancy of the light-sources and of the transmission-factors of the optical paths was made possible by removing the two colored glasses from the optical paths momentarily without altering the temperature conditions. The relative transmission-factors of the two pieces of the given specimen were measured throughout the range of temperature indicated and the results for ten commercial specimens are given in the diagram and in the table. (Fig. 1 and Table 1.)

TABLE 1.

Specimen.	Principal coloring element.	Color.		Relative transmission-factors at various temperatures (centigrade).				
		Cold.	Hot.	30°.	100°.	200°.	300°.	350°.
1	Copper	Medium red	.....	100	97	92	87	84
2	Cobalt	Light blue	.....	100	101	104	107	108
3	Cobalt	Deep violet	Deep blue	No appreciable change				
4	Gold	Pink	Violet	100	99	96	94	93
5	Copper	Blue-green	Yellow-green	100	98	94	87	82
6	Manganese	Purple	Blue-violet	100	97	94	91	90
7	.....	Lemon-yellow	Orange	100	94	84	75	71
8	.....	Dull yellow	.....	100	98	94	91	90
9	Copper	Deep red	.....	100	86	67	50	42
10	Chromium	Yellowish green	Yellow	100	95	84	72	67

No color-difference was encountered during the measurements except that due to a change in the spectral transmission charac-

teristic of the heated specimen. This color-difference became very marked for specimens 5 and 10. The transmission-factor of the hotter piece is given in terms of that of the colder piece of the same specimen at the various temperatures—that is, the transmission-factors as given are relative values and not absolute. The color of a specimen at the highest temperature is given as compared with that of a piece of the same specimen at 30° C, the change being sufficient to be readily described in

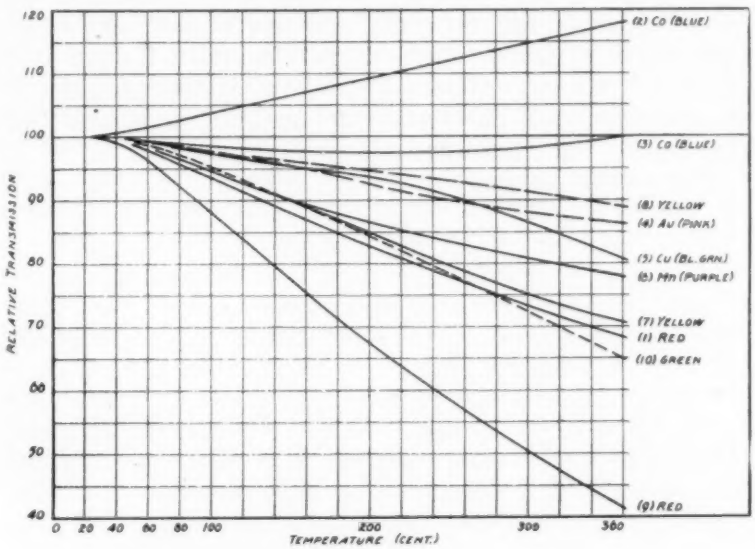

FIG. 1.

terms of our ordinary indefinite terminology. All the glasses excepting the two containing cobalt decreased in transmission-factor as the temperature increased, and in some cases this decrease in transmission-factor was very large. The curves obtained by plotting temperature and relative transmission-factor are, in general, approximately straight lines indicating that throughout this range of temperature the transmission-factor changes approximately proportionally with the temperature for the specimens used. Owing to the relatively slight change in hue in the red end of the spectrum, the red glasses 1 and 9 did not change

appreciably in color when heated, notwithstanding large decreases in their transmission-factors.

This preliminary study indicates an interesting field for careful research which might throw more light upon the question, "How are glasses colored?" It is the hope of the author to carry this investigation further. In the meantime, so far as general conclusions can be drawn from this series of glasses which covers a wide range, it appears that the transmission-factor of colored glasses generally is a function of the temperature within the range investigated. It will be noted that the highest temperature studied is below that at which the glass becomes self-luminous or plastic. It will be of interest to carry this investigation close to the melting point. The results obtained are of interest both theoretically and practically.

NELA RESEARCH LABORATORY,
CLEVELAND, OHIO,
July, 1919.

THE CONTROL OF THE SAGGER MIXTURE.

By V. S. Schory.

Manufacturers who fire wares in saggers are at times under the necessity of making changes in the sagger mixture. A common method of substituting a new clay for one previously in use is to make a visual examination of fired pieces of the various clays and from such an inspection to decide upon a new sagger mixture. This practice, depending partly on judgment based on insufficient data and partly on pure guess-work, is likely to prove expensive through loss of saggers and ware. Another method is to prepare a number of sagger mixtures in which one or more of the materials are varied and to study the saggers made of these mixtures. It is no doubt possible to judge roughly of the quality of a sagger by inspection and breaking with a hammer, but if accurate information is desired, it is necessary to select a group of say 25, 50 or 100 saggers and fire and re-fire them under standard conditions until all are broken, meanwhile keeping a record of their behavior. In this way a numerical expression for the quality of saggers from a given mixture can be obtained. This method requires considerable time and work and is not altogether inexpensive, expecially if some low-grade mixtures are made.

It is sometimes necessary to make a change in the sagger mixture on short notice, thus precluding the possibility of any such research as that mentioned above. This exigency has occurred more frequently during the last few years because of the abnormal conditions prevailing in the clay-mining industry and in transportation. The extensive re-adjustment of sources of supply, the congestion of freight, and the difficulties experienced by the clay shippers in securing the needed supply of cars, have resulted in unforeseen shortages in the clay bins. When the stock of one or more sagger clays is exhausted it may be necessary, in order to maintain the usual rate of production, to make a sagger mixture from the sagger clays remaining in stock. It

may not be possible to make a sagger of the standard quality from these materials but the problem at the moment is to produce the best sagger that it is possible to make from the clays available.

Under the stress of such circumstances it seemed desirable to devise some preliminary test that would serve as a guide in making a change in the sagger mixture. No attempt was made to formulate tests from which to absolutely predict the quality of the sagger. A great many variables affect the life of a sagger and not the least important of these are the inherent properties of the individual clays. So that, granting the feasibility of the scheme, it would require an extended research to formulate a series of tests that would give a numerical rating to any sagger mixture, applicable to all clays and combinations of clays. Instead, the purpose was to devise a preliminary test that would eliminate as much laborious experimenting as possible, but which would not supersede entirely the determination of the average life of a sagger by re-firing as mentioned above.

From the information available it is evident that the clay content of most sagger mixtures in factory practice consists of one or more dense-burning or vitrifying clays and one or more open-burning and comparatively refractory clays. This is not always the case. In some sagger mixtures the clay content is derived from a single clay or a mixture of clays, all of which resemble each other in vitrification behavior. If the clay content of a sagger mixture consists of one vitrifying and one open-burning clay, the proportions used should be such as to give the sagger satisfactory strength and refractoriness.[1] In the usual case if the content of open-burning clay is high, the resistance of the sagger to temperature changes is correspondingly great but the strength is low. In the extreme case the sagger is often of little value because of brittleness in the cold or because of deformation under load in the fire.

The relative importance of these two properties will vary in different factories. Some users require great resistance to changes of temperature; in other cases mechanical strength is more important. For any one use there is the desirable mean in which

[1] G. H. Brown, "Notes on Sagger Clays and Mixtures," *J. Am. Ceram. Soc.*, **1**, 716 (1918).

the properties are developed in proportion to their relative importance. An effort was made to locate this mean, approximately, by determining the degree of vitrification of satisfactory sagger mixtures.

A number of sagger mixtures that have given satisfactory results in factory practice were selected. The clay content of four of these consisted of clays that vitrified at or before cone 11, combined with clays which after firing to cone 11 absorbed between 6 and 10 per cent of water; the clay content of one mixture consisted of two clays that burned to low absorption but were not vitreous at this heat. Small batches of these mixes were weighed up, the grog being omitted in order to avoid any error that might arise from variations in the absorption of the grog particles. The batches were blunged, brought to the plastic condition, formed into bars, dried, and fired to cone 11, the regular sagger-kiln heat. The absorptions of the bars were determined by the increase in weight after boiling for three hours and soaking twenty-four hours in water. The absorptions in all cases were between 2.5 and 4 per cent.

Similar tests were made using the clay content of sagger mixtures that had proven unsatisfactory in use. These mixtures consisted of the same clays as were used in some of the satisfactory mixtures but the clays were combined in different proportions. Fired bars of these mixtures showed absorptions either greater than 4.5 per cent or less than 1.5 per cent.

The number of mixtures studied was too small to permit of drawing positive conclusions. However, within the limits of the study, no exceptions were found to the rule that mixtures of clays showing absorptions between 2.5 per cent and 4 per cent are superior to mixtures of the same clays having absorptions much less than 2.5 per cent or greater than 4 per cent. These data classified the sagger batches that had been used in an emergency when there was no time for experimenting and had later proven inferior in quality. It was, therefore, decided to base future work on these results until exceptions to the rule occurred. By experiment the proportions of each two sagger clays that gave mixtures burning to an absorption of approximately 3.25 per cent

were determined. From these data a sagger mixture is planned immediately in case the supply of one clay is exhausted.

The absorption determination is also used as a preliminary to making a study of a new sagger clay. The new clay is mixed with a standard open-burning clay or a standard vitrifying clay in such proportions that the absorption of the resulting pieces is approximately 3.25 per cent. This mixture is then used as the clay content of a sagger batch and the average life of a sagger is determined by re-firing a given number until all are broken. This figure is taken as a measure of the value of the new clay.

This method of control of the sagger mixture is very simple and has proven useful in factory practice. It is presented for the consideration of other users of saggers who may at times be under the necessity of changing their sagger mixtures. The degree of vitrification represented by the figures for absorption is not given as a generalization. Individual users may secure better results with a greater or lesser degree of vitrification than that mentioned above.

STANDARD SANITARY MFG. CO.,
TIFFIN, OHIO.

CERAMIC ABSTRACTS.

General.

Rapid method of determining magnesium. F. W. BRUCKMILLER. *The Chemist-Analyst, J. T. Baker Chemical Co.*, p. 7, Jan. (1919).—Remove the silica and calcium in the usual manner and after evaporating to dryness, to get rid of the excess ammonium salts and filtering, proceed as follows: Make up the filtrate to at least 100 cc. volume and make distinctly alkaline with NH_4OH. Cool by placing the beaker into ice water and then add an excess of microcosmic salt solution. Stir vigorously and for some time until the magnesium has all come down and then add 10 cc. of NH_4OH. The more the stirring the better will the precipitate settle and the sooner will it be ready to filter. Filter through a suitable filter paper and wash by decantation several times using 3 per cent ammonia water. It is not necessary to wash the beaker clean, for the contents of the filter paper are washed by means of hot water into the beaker in which the precipitation took place and the whole solution boiled until the ammonia is driven off. Methyl orange indicator is added and the solution titrated with a standard solution of HCl. The strength of the solution used will depend upon the quantity of magnesium present. The following factors will convert cubic centimeters into grams of magnesium:

1 cc. 0.10 *N* HCl	0.00120 gm. Mg
1 cc. 0.05 *N* HCl	0.00060 gm. Mg
1 cc. 0.02 *N* HCl	0.00025 gm. Mg

C. TREISCHEL

Notes on the perchloric acid method for potash in cement materials. W. B. NEWBERRY. *The Chemist-Analyst*, pp. 8–11, Jan. (1919).—*For total potash:* Grind $^1/_2$ gram sample (flue dust, shale, etc.) with $^1/_2$ gram ammonium chloride in an agate mortar. Add 4 grams of pure calcium carbonate and grind thoroughly together. Put a little calcium carbonate in the bottom of a J. Lawrence Smith crucible, add the charge with 1 gram calcium carbonate on top, cover and heat with a low flame till there is no further odor of ammonia (15 minutes). The heat must not be high enough to permit the escape of visible fumes. Then raise the heat to moderate redness for 45 minutes, turning crucible occasionally. Cool, dissolve the melt in a little water, carefully rinsing the crucible. Slake on water bath, breaking up lumps. Filter off excess calcium carbonate, wash and make filtrate strongly acid with HCl. Boil and add slight excess of barium chloride. Let stand preferably several hours. Filter off the barium sulphate, wash, heat the filtrate to boiling and add ammonium carbonate until no further precipitate forms. Add a few drops of ammonium oxalate, filter and wash. Evapo-

rate to dryness in a platinum dish and when dry heat carefully to just below redness till all ammonium chloride fumes are gone. Cool, dissolve in 25 cc. hot water, filter off anything undissolved and add to the filtrate enough 60 per cent perchloric acid solution to convert all the alkali metals into perchlorates (ordinarily 1 cc. is enough). Evaporate until nearly dry and when heavy fumes of $HClO_4$ appear, cool, add 25 cc. hot water, another cc. perchloric acid, and evaporate again to the same point. Cool, add 25 cc. wash-alcohol (containing 1 cc. perchloric acid solution to every 300 cc.), filter on asbestos in a Gooch crucible, wash with the same alcohol, dry and weigh as $KClO_4$. In washing the precipitates it is unnecessary to wash them entirely chlorine-free; for ordinary work 3 or 4 washings are sufficient. The barium chloride, ammonium carbonate and ammonium oxalate mentioned are all used in saturated solutions.

For water soluble potash: Five grams of the sample are boiled thirty minutes with 150 cc. water in a small flask with condensing tube. Cool, make up to 250 cc., mix well and filter through a dry paper without washing. Take 50 cc. of the filtrate corresponding to one gram of the sample, acidify strongly with HCl and proceed as in the determination of total potash given above. Multiply weight of potassium perchlorate found by 33.935 for percent of K_2O in sample. C. TREISCHEL

Geological.

Ball clays of West Tennessee. ROLF A. SCHROEDER. *The Resources of Tenn.*, **9**, No. 2, April (1919).—High-grade ball clays are found in abundance in Henry and Carroll Counties and sparingly in Haywood and Madison counties. South of these counties clay strata are abundant but are less pure and contain quartz, mica and iron compounds. The best ball clays of Henry and Carroll counties are apparently associated with lignite. The clays of West Tennessee are in the form of lenses which are found in the upper portions of the Ripley sand (Upper Cretaceou.) and the lower Lagrange sand (Eocene). According to Schroeder some of the more important uses of ball clay are as follows: (1) *Electric porcelain ware and insulators.* (2) *Porcelain or china.* (3) *Glass pots for optical glasses.* (4) *Sanitary ware and enamel ware.* (5) *In making "graphite crucibles, as a binder in abrasive wheels, in making green-house wares, tiling, lead pencils, chemical ware and cosmetics."* The report contains many descriptions of localities arranged by counties. Many of the clays were tested at the Ceramic Laboratory of the University of Illinois under the direction of Prof. C. W. Parmelee. The results of these tests and the descriptions of prospects and worked pits are too numerous to be considered here. The original report is especially worthy of consideration by any who may be interested in the clays of the region involved. E. D. ELSTON.

Annual report on the mineral production of Canada, 1917. Dept. Mines, Mines Branch, Ottawa (1919).—A series of tables shows the domestic production and imports of clay and clay products. In addition the production of clay products by provinces is stated. E. D. ELSTON.

Preliminary report of the mineral production of Canada, 1918. Can. Dept. Mines, Mines Branch, Ottawa, Feb. 27, 1919.—The report is interesting, in that it shows the increase or decrease in production, as the case may be, with respect to the various materials. According to this preliminary set of statistics for 1918, a decrease of $179,203 is shown for clay products.

E. D. ELSTON.

Mineral production of the United States in 1916. H. D. MCCASKEY AND MARTHA B. CLARK. U. S. Geol. Surv., *Mineral Resources, 1916.* Part I, *A*, June 28, 1919.—A brief résumé of the value of clay and clay products and the value of imports of such materials is to be noted in this publication. The mineral production by states is given in tabular form and it is also worth while to note that a statement dealing with the mineral products of the United States in 1916 in order of value is included. In this statement clay products are given fifth place and raw clay is cited as twenty-seventh in value. For further details in connection with the numerous tabulated statements the reader is referred to the original publication. E. D. ELSTON.

Magnesite: its geology, products and their uses. C. D. DOLMAN. *Am. Inst. Min. and Metal. Engrs.*, **152,** 1913 (1919).—In 1913, about 200,000 tons of magnesite were consumed in the United States, less than 3% of this amt. being produced at home. In 1918 there were produced and used in the United States 225,000 tons. The material produced and sold in the United States must contain in the crude form, no more than 3.5% SiO_2 and 2% CaO, and in the dead-burned product not more than 7% SiO_2, 4% CaO, and 8% Fe_2O_3 plus Al_2O_3. There are two principal sources of magnesite in the United States; California, and Stevens County, Washington. The California magnesite is similar to the Grecian, being amorphous and occurring in serpentine rocks. The Washington deposits are similar to the Austro-Hungarian and Canadian ores and are of the massive crystalline variety. Below are given typical analyses:

	MgO.	CaO.	CO_2.	SiO_2.	FeO.	Fe_2O_3.
Napa County, Cal.....	45.01	0.67	50.65	1.99	1.49	
Grecian magnesite.....	45.75	1.44	49.88	1.63		1.36
Stevens County, Wash.....	45.20	1.74	49.70	1.85	0.88	
Austro-Hungarian magnesite.	43.82	0.97	50.44	0.45		3.65

With a production of 110,000 tons of crude ore from June, 1918, to April, 1919, only 20%, or one ton in five, mined at the quarries of the Northwest Magnesite Co., in Washington, was waste, whereas, in the Austro-Hungarian quarries it is necessary to mine and sort five tons of crude ore to produce one ton of finished product. Thus with close sorting a product just as pure, if not more pure than the foreign material, may be obtained. Geological surveys indicate that there are 7,000,000 tons of magnesite in the Stevens

County district, and exploratory drilling may multiply this estimate many fold. The deposits occur as a replacement of lenses of dolomite in sedimentary rocks, probably of pre-Cambrian age. The greatest use for magnesite is in the basic open-hearth process of making steel. It is used in furnace bottoms, soaking pits, metal mixers, billet and bar heating furnaces, copper converters, and in many types of furnaces. The magnesite burned to 1200° C is called "calcined magnesite," that burned much harder is called "dead-burned." Ferro-magnesite is made by the careful grinding and mixing of iron ore with the raw magnesite and burning to a sintering temperature. Magnesite is now put to many uses, some of which are as follows: refractory porcelains, lining for electric furnaces, composition flooring, stucco, and other oxychloride cements, boiler and steam-pipe insulation, for the production of Mg metal for important new alloys with Al and Pb, for production of $MgSO_4$, $MgCl_2$ and $Mg(OH)_2$. F. A. KIRKPATRICK.

Refractories.

Experiments on silica brick. M. PHILIPON. *Rev. de Metal.*, **15**, 51 (1918).—Four different materials having the following compositions were used:

	1.	2.	3.	4.
SiO_2	97.20	97.00	96.30	97.60
Al_2O_3	0.78	1.82	2.40	0.95
Fe_2O_3	0.37	0.60	0.40	0.52
CaO	0.90	0.00	0.28	0.00
MgO	0.00	0.00	0.00	0.00
Ignition loss	0.60	0.50	1.00	0.80
Fusion temp. ° C	1770	1780	1790	1770

1. White quartz from the Central Plateau.
2. Normandy quartz.
3. Sandstone from Pas-de-Calais.
4. Amorphous silica from Allier.

The materials were ground and separated into portions of different size of grain, the average size of grain of each portion being used in interpreting the results. $1^1/_2\%$ of CaO was used. Water was added and the mixtures ground wet for 10 mins. and molded into ordinary-sized brick. These were dried on iron plates at 100° C and burned to 1300° C, the conditions being kept alike in all the tests.

The results obtained are shown in the following tables:

TABLE 1.

Showing Effect of Size of Grain on Compressive Strength of Brick Burned to 1300° C. Figures by Interpolation from Author's Fig. 2.

Diameter of grains in mm.	Nearest corresponding mesh of Tyler standard testing sieves.	Compressive strength. Kg. per sq. cm. 1.	2.	4.
0.05	300	250	300	210
0.06		140	230	80
0.07	200	50	150	25
0.08		23	80	5
0.09		14	55	
0.10	150	8	37	
0.12		5	20	
0.14		3	10	
0.16			5	
0.18	80		4	

No mixtures of different sizes were used.

TABLE 2.

Showing Effect of Amount of CaO on Compressive Strength of Brick after Burning to 1300° C. By Interpolation from Author's Fig. 5.

% CaO.	Crushing Strength, kg. per sq. cm. No. 1.	2.	3.
0	50	110	
0.5	172	208	147
1.0	278	270	220
1.5	310	290	253
2.0	304	287	263
2.5	262	252	257

TABLE 3.

Effect of Amount of Water on Strength of Brick of Material Passing 200-Mesh Sieve.

% Water.	Compressive strength after drying. Kg. per sq. cm.	Compressive strength after burning to 1300° C. Kg. per sq. cm.
15	12	180
16	13	195
17	15	190
18	15	220
19	17	250
20	19	265
21	20	270

TABLE 4.

Effect of Amount of Lime on Fusion Temperature.

% CaO.	0.	0.5.	1.0.	2.5.
Quartz III	1790	1780	1750	1740
Quartz I	1770		1760	1730

TABLE 5.

Effect of Size of Grain and Amount of Lime upon Various Properties.

		Compressive strength. Kg. per sq. cm.	Per cent expansion.	Porosity.
Quartz 1	A	270	1.2	18.0
	B	285	1.4	18.6
	C	243	1.5	17.7
	D	194	1.6	16.2
Quartz 2	A	242	1.1	22.0
	B	223	1.1	19.3
	C	225	1.2	18.5
	D	205	1.3	17.0
Quartz 3	A	200	1.3	21.0
	B	228	1.5	19.8
	C	175	1.4	19.0
	D	165	1.5	18.2
Quartz 4	A	194	1.4	20.5
	B	171	1.5	19.7
	C	155	1.6	17.8
	D	138	1.8	15.9

	Per cent passing 200 mesh.	Per cent grains 2 to 8 mm.	Per cent CaO.
Series A	60	40	1.2
B	50	50	1.0
C	40	60	0.8
D	30	70	0.6

F. A. KIRKPATRICK.

Cement and Lime.

Cements producing quick-hardening concrete. P. H. BATES. *Concrete* (Cement Mill Section), **15**, 9 (1919). *Presented at the 1919 meeting of the American Society for Testing Materials.*—In the course of investigations which the Pittsburgh branch of the Bureau of Standards has been conducting in portland cement and related problems, there has been produced a quick-setting sorel-cement concrete which obtains the greater part of its strength in 24 hours. Tests were first made of mortar having the composition of so-called "composition flooring" much used in office buildings, passenger cars, and other places. Such a mortar has been successfully used as a stucco. Cali-

fornia magnesite was used. The specimens were composed of 50% magnesia, 12% asbestos, 10% sawdust, 22% ground sand, and 6% iron oxide, all by weight. This mixture was gauged with 52% of a solution of magnesium chloride having a gravity of 1.885 (about 93° Baume). Analyses are as follows:

	Oxide, per cent.	Chloride, per cent.
SiO_2	5.14	
Al_2O_3	0.78	
Fe_2O_3	0.57	
CaO	5.69	0.20
MgO	85.01	9.24
K_2O		0.17
Na_2O		0.70
Cl		16.54
Ignition loss	2.86	

Tension specimens were of the forms specified in the A. S. T. M. "Standard Specifications and Tests for Portland Cement." Compression specimens were 2 inch by 4 inch cylinders. The following strengths in pounds per square inch were obtained:

	Specimen.	24 hours.	7 days.	28 days.	90 days.
A	Tension	531	841	1087	1034
	Compression	2240	3795	5300	4340
B	Tension	576	900	935	1049
	Compression	2900	4240	5300	5370

This mortar was used in making a concrete. The strength of this concrete and also the compressive strength developed by a portland cement concrete using the same proportions of the same aggregates are given in Table 1.

As the magnesia weighed but 51 lb. per cu. ft., the actual percentage by weight of the magnesia in any one concrete was decidedly less than the percentage of Portland cement. For this reason the 1 : 6 concrete was proportioned both by weight and by vol. when the magnesia was used as the cementing material. All specimens were stored in the air until broken. The gravel used was obtained from the Allegheny River and was screened between a $1/8''$ and $1\,1/2''$ screen. It contained an excessive amt. of the finer sizes. The limestone was a rather soft stone screened between the $1/4''$ and $1''$ screens. The "coarse sand" aggregate was sand from the Allegheny River screened between the $1/8''$ and $1/4''$ screens. As the information sought had to do alone with early strengths, specimens were made for breaking at 24 hrs., 48 hrs. and 7 days, in the case of those made with magnesia, and 48 hrs. and 7 days when Portland cement was used. The results show that the Sorel-cement concretes, with but two exceptions, have a strength at 48 hrs. greater than that obtained by the use of Portland cement in 7 days. However, it is also seen that there is in general but little increase in the strength of the

TABLE 1.

Comparison of Compressive Strengths of Sorel and Portland Cement Concretes.

6″ × 12″ Cylinders. Strengths in Pounds per Square Inch.

Proportions by volume.	Percentage of cement by weight.		24 Hours.		48 Hours.		7 Days.		Per cent H_2O in Portland-cement concrete.	Per cent $MgCl_2$ in Sorel cement concrete.
	Portland.	MgO.	Portland.	MgO.	Portland.	MgO.	Portland.	MgO.		
Gravel aggregate.										
1 : 0.5 : 1.5	33.3	20.3	....	1740	1570	3490	2965	2910	12.1	14.7
1 : 1.0 : 3.0	20.0	11.3	....	1705	1115	2260	2020	2850	7.8	9.5
1 : 1.5 : 4.5	14.3	7.8	....	1755	680	2145	1430	2240	7.9	9.8
[a] 1 : 1.5 : 4.5	....	14.3	....	2880	....	3315	....	2720	....	12.1
Limestone aggregate.										
1 : 2/3 : 1 1/3	35.2	21.8	....	2985	2260	3990	3930	4320	12.2	18.5
1 : 1 1/3 : 2 2/3	21.4	12.2	....	1940	1340	2805	2990	2970	9.9	13.7
1 : 2 : 4	15.4	8.5	....	1935	655	2330	1755	2480	9.5	12.8
[a] 1 : 2 : 4	....	15.4	....	3270	....	4020	....	4320	....	13.7
Coarse-Sand aggregate.										
1 : 0.5 : 1.5	34.0	20.8	....	2060	1715	2570	3270	2735	13.2	20.0
1 : 1.0 : 3.0	20.6	11.6	....	1910	545	2225	1635	2430	11.4	16.0
1 : 1.5 : 4.5	14.7	8.0	....	935	325	1695	985	1870	11.4	14.7
[a] 1 : 1.5 : 4.5	....	14.7	....	2355	....	3260	....	3190	....	15.7

NOTE.—The percentage by weight of MgO in 1 : 0.5 : 1.5 and 1 : 2/3 : 1 1/3 is but very little greater than the percentage by weight of Portland cement in 1 : 1.0 : 3.0 and 1 : 1 1/3 : 2 2/3, respectively.

[a] MgO proportioned by weight, making weight percentage of MgO equal weight percentage Portland cement in 1 : 1.5 : 4.5 and 1 : 2 : 4.

former between the 48-hr. period and the 7-day period. The results obtained at all periods from the Sorel cement concrete proportioned by wt. are generally higher than those obtained when the proportioning was done by vol., regardless of what the proportions were. This clearly shows that for such a light material the proportions should be decidedly different from those generally used with Portland cement. It would seem as if too much magnesia was used in the rich concretes and too little in the lean ones when the proportioning was carried out by vol.

Attention should be called to the difference in the manner in which the hardening of the two concretes takes place. In a Portland-cement concrete, the cement hardens by the action of the added water. During the process of hardening it is immersed in an atmosphere containing in a greater or less degree one of the essential elements of the process, that is, water, either as a liquid or vapor. On the other hand, in the Sorel cement concrete the hardening takes place as a result of the action of the chloride on the oxide. The chloride is always essential but any deficiency, as for instance the use of a too dilute solution, or any marked excess, is injurious. Therefore, not only the ratios between the aggregate and the magnesia must be studied, but also the ratio between the chloride and the magnesia.

While the results do show the lack of proper proportioning of both the magnesia and the chloride, yet these poorly proportioned concretes show in 24 hrs. as high strengths as the more properly proportioned Portland cement concretes show in seven days. Another point should be remembered in regard to these Sorel cement concretes, that is, they cannot be frozen. Temps. below freezing will retard the hardening to a degree, but the freezing point of the solution is so low that no care need be taken to prevent damage from low temps. The remainder of the discussion concerns the properties of calcium-aluminate cements and concretes, previously published in THIS JOURNAL, **1**, 679 (1918). F. A. KIRKPATRICK.

New wet process plant of Nebraska Cement Company. D. C. FINDLAY. *Concrete* (Concrete Cement Mill Section), **15**, 1 (1919).—The plant, located at Superior, Neb., has a maximum capacity of 3,000 barrels per day. All buildings, storage tanks, slurry elevators, and every unit that could be advantageously built so, were made of reinforced concrete. Soft, yellow limestone and blue clay are dug by steam shovel and hauled by locomotives $2^1/_2$ miles to the plant. The materials are reduced by a 38″ by 60″ Fairmont crusher, then ground into slurry in "Compeb" ball mills. The slurry is discharged into any of three reinforced concrete correcting basins holding about 200 barrels of slurry. The latter is analyzed and drawn from the basins in proper proportions into a Smidth type mixing basin of 1,000 barrels capacity. When the resulting mix is absolutely correct it is drawn off into any of three storage basins, two of which are 26 feet in depth and hold 1750 barrels each, and one 16 feet in depth holding 1,000 barrels. The slurry is then elevated into storage basins above the kilns and fed by means of Link-Belt "S" type slurry feeders. The three rotary kilns are 8 feet in diameter and 200 feet long.

The kind of inside lining is not stated. The kilns are fired with powdered coal. The clinker passes into two 60-foot rotary coolers, then into four storage bins 26 feet in diameter and 45 feet high. At this point, gypsum is added and the product ground in five 57-inch Fuller mills and is then elevated to the storage bins. There are 10 bins, each 26 feet in diameter and 80 feet high with walls 7 feet thick, the total capacity being 100,000 barrels. The entire plant is motor driven, there being in all some 50 motors in service. The power plant is equipped with a 1500 kw. Westinghouse steam turbine with Le Blanc condenser, and a 2000 kw. Allis-Chalmers turbine and a jet condenser. Steam is supplied by four 450 h. p. water tube boilers equipped with Taylor forced-draft stokers. F. A. KIRKPATRICK.

CERAMIC PATENTS.

G. E. MIDDLETON, ABSTRACTOR

Truck for tunnel kilns. C. H. ZWERMANN. U. S. 1,306,160, June 10, 1919. The frame of this truck is of channel irons. Upon this frame is a sheet metal platform upon which rests a series of transverse I-beams embedded in kieselguhr. The platform proper which rests upon these I-beams is composed of overlapping, interlocking fire-clay blocks. As these blocks become worn they can be replaced.

Tunnel kiln. C. H. ZWERMANN. U. S. 1,306,161, June 10, 1919. This is a twin-tunnel muffle kiln, the two tunnels being parallel and having a common inner wall. The ware in one passes in a direction opposite to that of the ware in the other, thus effecting a mutual cooling and preheating through the medium of a specially designed central wall in the end portions of the kiln. The combustion chambers extend longitudinally of the tunnels, the walls thereof being of relatively thin plates of carborundum capable of withstanding great heat and at the same time readily transmitting it. The ring is longitudinal. The fuel is either oil or gas.

Brick-mold-handling apparatus. I. C. FREY. U. S. 1,306,477, June 10, 1919. This apparatus comprises synchronously operating, divergently moving conveyors for separating a mold from its contents, means for moving the emptied mold to a sander by which it is coated with a regulated quantity of sand, turning the sanded mold to the upright or filling position and automatically returning the mold to the filling chamber of a brick machine.

Glass-matting process. T. UEDO. U. S. 1,306,505, June 10, 1919. A paste is made comprising active ingredients, such as basic alkali silicates, basic lead silicates, lead oxides, plumbates and lead borates; inert ingredients, such as pulverized highly refractory material, for example, burned porcelain, burned stoneware, fire clays, quartz, etc.; and a binder, such as boiled starch, gum, glue, etc. This is painted in appropriate design upon the glass surface to be matted and the whole placed in a furnace and heated at a temperature higher than the softening point of the glass for a time sufficiently long to

effect a fluxing action upon the glass by the active ingredient. The glass is then cooled and treated with any ordinary strong mineral acid. During the heating the active ingredients combine chemically with a thin surface layer of the softened glass forming a new combination, which, on account of the presence of the inert materials, can be easily decomposed and removed by an acid, thus effecting the matting. The inert materials function principally to prevent the active materials and the reaction products from sticking so fast to the glass surface as to make their decomposition by the acid difficult.

Process of drawing glass cylinders. W. WESTBURY. U. S. 1,306,651, June 10, 1919. During the elevation of the bait a complete air circuit is maintained within the cylinder being drawn, said circuit including downwardly and upwardly flowing air currents, the upward current coming into contact with the surface of the cylinder.

Glass-stowing tool. J. A. BECHTEL. U. S. 1,306,993, June 17, 1919. A reversible stowing tool having its blade or that portion which comes in contact with the glass of greater length than the linear dimension of that edge of the glass plate with which the tool contacts.

Glass-delivering and melting apparatus. E. ROIRANT. U. S. 1,307,150, June 17, 1919. Molten glass is collected from a furnace by means of a receptacle which is swung from position under the delivery end of the furnace to the gathering device and back again. During this operation the glass in the receptacle may be kept molten by passing an electric current through it.

Magnesia brick and method of making the same. H. H. HANSON. U. S. 1,307,197, June 17, 1919. Calcined magnesite or magnesia, 83%, is mixed with 17% fireclay, then a small amount of sodium silicate and water is added and the whole thoroughly mixed in a pug mill. It is then formed into bricks subjected to a pressure of six tons per square inch, and then subjected to 1600° C. The product is said to be a practically non-porous, basic brick expanding very little when heated to high temperatures.

Splitting buck for glass cylinders. J. MURPHY. U. S. 1,307,209, June 17, 1919. This buck has two sets of supports, one consisting of flexible strips of fabric for holding the cylinder during splitting and another consisting of two sets of anti-friction rollers, one set at each end of the buck, which may be raised to lift the cylinder from the first-mentioned supports and to permit of its being rotated for inspection preparatory to splitting.

Apparatus for the manufacture of plate glass. H. K. HITCHCOCK. U. S. 1,307,357, June 24, 1919. By means of this apparatus the use of tank furnace glass for the manufacture of plate glass is said to be rendered practical and economical. The operation of the apparatus by which the glass is caused to flow from the tank to the casting-table is automatically controlled by the movement of the table itself below the glass delivery spout.

Window-glass-blowing head. W. E. STANDLEY. U. S. 1,307,381, June 24, 1919. The construction of this head enables the flow of air to and from the hollow bait to be regulated to maintain a uniform pressure within the hollow cylinder.

Machine for fire-finishing tumblers and other glass articles. H. H. PITT. U. S. 1,307,453, June 24, 1919. Means are provided for passing water, steam, air or other cooling medium through the plugs or stands which support the hollow glass articles being fire-finished, thereby cooling the interiors of the articles and preventing their sticking to the plugs.

Glass furnace. F. L. O. WADSWORTH. U. S. 1,307,527, June 24, 1919. This furnace is designed to deliver in an upward direction a constant stream of molten glass under a gravity head in such condition that open-bottomed receptacles may be successively brought into register with the delivery opening to receive comparatively small quantities of molten glass and when withdrawn the flow of molten glass will continue and will fall away from the orifice.

Heat insulating composition. F. A. HEADSON. U. S. 1,307,548, June 24, 1919. Calcined diatomaceous earth, 75%, finely divided or fibrous asbestos either calcined or raw, preferably the former, 25%, either with or without a binder of refractory or bonding clay amounting to 3% to 10% of the combined diatomaceous earth and asbestos. This composition is molded in any desired shape and burned at from 2000° F to 3000° F for six hours.

U. S. 1,307,549 discloses substantially the above.

Utilization of cement-kiln dust. R. J. NESTELL. U. S. 1,307,920, June 24, 1919. Cement-kiln dust, which sometimes contains as high as 13% K_2O, nearly all water soluble, is rendered suitable for use as a crude fertilizer by first mixing it with water and then passing hot kiln gases containing CO_2 through the mixture in such a manner as to increase the solubility of the potassium compound and to carbonate any free lime present.

Glass-drawing apparatus. W. WESTBURY. U. S. 1,307,943, June 24, 1919. By the use of this apparatus a cylinder may be formed from a charge of glass taken from the melting furnace, drawn from a pot which closes or seals the drawing opening and in which the charge of glass is exposed to atmospheric cooling while protected from the heat of the furnace.

U. S. 1,307,946 discloses substantially the above. The claims are drawn to the process.

Brick-carrier. W. H. ALLEN. U. S. 1,308,021, July 1, 1919. By means of this device a number of bricks can be transferred from a stack or kiln to a car or *vice versa*, thereby eliminating manual handling.

Tile press. F. B. YINGLING. U. S. 1,308,213, July 1, 1919. A toggle-operated dry-press having a reciprocating charging hopper comprising means for agitating the clay therein. The surfaces of the dies are automatically cleaned by means of a brush supported by the charging hopper.

Glass-bait. G. C. DEBAY. U. S. 1,308,278, July 1, 1919. The necessity for submerging this bait in the molten glass to start the draw is avoided by the use of a suction means which draws the glass up into an annular cavity in the bottom of the bait. Means are also provided for relieving the strain on the glass cylinder due to cooling and contracting.

Glass-carrying rod for glass-annealing leers. J. W. CRUICKSHANK. U. S. 1,308,337, July 1, 1919. This carrying rod or lifting bar is designed to be of low conductivity and thus avoid either chilling or heating the sheet of glass being annealed. The bar is made of two angle irons riveted together and carrying between them a strip of asbestos projecting beyond the working faces of the irons.

Glass-flattening oven. H. E. DEVAUGHN. U. S. 1,308,341, July 1, 1919. The driving mechanism of this flattening oven is outside and above it and the rotary wheel is suspended from a support located at a point such that the temperature of the oven can have no detrimental effect upon the operation. The making of repairs is thus expedited.

Process and apparatus for making glass plate letters. A. W. GAST. U. S. 1,308,408, July 1, 1919. Glass-plate blanks of the desired size are passed through a longitudinal heating chamber upon suitable supports and when attaining the proper temperature are impressed by means of a heated pneumatic die. The formed blank is then passed through the remaining length of the longitudinal chamber and slowly cooled.

Treatment of clays and earths. F. LANGFORD. U. S. 1,308,429, July 1, 1919. This process relates to the production of aluminum and aluminum compounds and comprises providing a wet mixture of comminuted wood of the California Redwood or *Sequoia sempervirens* together with the earthy material, clay or ore to be treated, adding to this mixture sulphur-oxygen compounds to produce a solvent solution containing H_2SO_4 to take up the undesirable impurities without dissolving the aluminum content of the mixture, separating the insoluble aluminum content from the solution, treating the insoluble aluminum residue with H_2SO_4 to form a solution of sulphates and an insoluble residue, separating the solution of sulphates from the insoluble residue and roasting the sulphates to provide the sulphur compounds for the treatment of the mixture of wood and earthy materials.

Protecting refractory furnace-linings. H. T. CHAPPELL. U. S. 1,308,481, July 1, 1919. Refractory furnace linings containing silica are protected from fusion and disintegration by supplying finely-divided calcined and leached alunite to such linings when they are at such a temperature as to be soft and partly fused.

Process of molding lenses. E. D. Tillyer and H. H. Styll. U. S. 1,308,820, July 8, 1919. Ophthalmic lenses are formed by first heating the glass blank, moistening the surfaces of the mold, placing the glass blanks between the mold sections while in a heated condition and then molding. The vapor films thus formed act as cushions preserving the fire polish of the glass while it is being shaped.

Process of treating lime. C. Catlett. U. S. 1,308,931, July 8, 1919. Lime is slacked, preparatory to making lime plaster or mortar, by adding sufficient water and up to about 5 per cent of an oxychloride of calcium, magnesium or zinc, or mixtures thereof. The resulting plaster is said to be hard, tough and relatively free from any tendency to blister or check after application.

Cement composition and method of preparing it. C. Catlett. U. S. 1,308,932, July 8, 1919. Relatively high, early-time strengths are developed in Portland cement mortars or concretes by the addition of not substantially more than 10 per cent of an oxychloride of calcium, magnesium or zinc, or mixtures thereof.

Continuous tunnel kiln. C. H. Zwermann. U. S. 1,308,973, July 8, 1919. A twin tunnel kiln, the two tunnels having a common inner wall. The ware passes in opposite directions in the two tunnels. The construction and operation of this kiln is somewhat similar to that of U. S. 1,306,161. The method of firing and controlling the draft is, however, quite different, this being an open fire kiln and similar to U. S. 1,275,352.

Sandless concrete. C. H. Light. U. S. 1,309,038, July 8, 1919. A sandless concrete which consists of sawdust 8 parts, cement 4 parts, plaster of Paris 1 part, and lime 1 part.

Glass blower. E. O. Whitley and E. L. Knowlton. U. S. 1,309,166, July 8, 1919. A glass-blower designed so that a plurality of tumblers may be drawn and blown at the same operation.

Glass apparatus. R. W. Hilton. U. S. 1,309,199, July 8, 1919. Means are provided in a glass furnace for supporting and shifting the pots in such a manner that when one pot is in position for the drawing of the cylinder, another pot will be in position for draining.

Kiln-furnace. R. W. Menk. U. S. 1,309,213, July 8, 1919. This furnace is shown in use on a downdraft kiln. The furnace consists of two parts, one without the kiln wall proper, the other within the bag wall. After the fire is started on the outer grate bars, the burning fuel is pushed back on grate bars within the bag walls. Within the outer furnace there is a removable corrugated, fire-clay liner tapering downwardly and outwardly so designed to prevent any "bridging" of the fuel. The draft enters above the fuel bed in the outer furnace and passes downwardly therethrough.

Process of drawing glass. J. A. CHAMBERS. U. S. 1,309,274, July 8, 1919. After a cylinder is drawn and removed a stump of hardened glass remains in the drawing ring. This patentee remelts this preparatory to a second draw by pouring molten glass through the drawing ring, this molten glass being of a higher temperature than the glass in the drawing part of the tank.

Concrete. A. MARKS. U. S. 1,309,296, July 8, 1919. A concrete consisting of Portland cement 2 parts, sawdust 1 part, sodium silicate solution sufficient to dampen and a calcium chloride solution or some easily ionized acid in such quantity that there shall be a slight excess of sodium silicate.

NOTE.—Copies of the above patents may be secured for five cents each by application to the Commissioner of Patents, Washington, D. C.

ACTIVITIES OF THE SOCIETY.

The following program will be presented on Ceramic Day, Wednesday, September 24th, at the Fifth National Exposition of Chemical Industries, Chicago, Illinois, week of September 22nd:

10:00 A.M.

"The American Ceramic Society—Past, Present and Future," Charles F. Binns.

"Buy on Analysis," Alexander Silverman.

"Superior Refractories," Ross C. Purdy.

"The Making of Pottery," Frederick H. Rhead.

"Some Aspects of Scientific Research in Relation to the Glass Industry," E. W. Washburn.

2:30 P.M.

"General Types of Optical Glass," Robert J. Montgomery.

"Brick and Tile," Douglas F. Stevens.

"The Application of Scientific Methods to Ceramic Research," A. V. Bleininger.

"The Manufacture of Optical Glass," J. C. Hostetter.

"Enameling Technology," R. R. Danielson.

"Fused Sillimanite Products," A. Malinovszky.

8:00 P.M.

Three films on ceramic subjects will be included in the motion pictures presented at the evening session.

NOTICES OF GLASS DIVISION.

Mr. Kerr has appointed the following committeee to be known as the "Central Committee of the Glass Division" to hold office until the next annual meeting of the Society: Mr. W. M. Clark, *Chairman*, Dr. S. R. Scholes, Dr. E. W. Washburn, Dr. J. C. Hostetter, Mr. R. L. Frink, Mr. F. A. Kirkpatrick, and Mr. C. O. Grafton. The duties of this Committee will be to perfect the organization of the Glass Division and to take action on such matters as may be referred to Committees.

The Society of Glass Technology of England has accepted the invitation of the Glass Division to be present at our Summer meeting in 1920. Dr. W. E. S. Turner, Secretary of that Society, is expecting to visit the States during September.

A meeting of the Glass Division was held in Cleveland on August 7th, during the Summer Session of the Society. Twenty members were present. It was voted that "Questions concerning every-day glass practice be submitted to the Central Committee and that it be instructed to hand these to men who in their minds are best able to discuss them, and that the discussions be published in the JOURNAL."

The following changes of address are noted:

C. C. Rand, Nela Park, Cleveland, Ohio.

J. C. Hostetter, Corning Glass Works, Corning, N. Y.

E. W. TILLOTSON, *Secretary*,
Glass Division

AMERICAN CERAMIC SOCIETY.

Acquisition of New Members during August, 1919.

Resident Associate.

Bloxsom, John J., Brookville Glass and Tile Co., Brookville, Pa.
Blumenthal, George, Jr., Bureau of Standards, Pittsburgh, Pa.
Brann, Albert, Ph.D., 220 Springdale Rd., East Orange, N. J.
Garrod, Fred. B., Owens Bottle Co., Toledo, Ohio.
Goebel, J., Jr., S. Highland Ave., Nyack, N. Y.
Hintze, T. Forsyth, 120 Liberty St., New York City.
Hollingsworth, C. M., Ohio Valley Clay Co., Steubenville, Ohio.
Holmes, J. C., Sandusky Bulb Works, Sandusky, Ohio.
Koerner, Walter A., Edison Lamp Works, Harrison, N. J.
Little, E. C., Laclede-Christy Clay Products Co., 1366 Peoples Gas Bldg., Chicago, Illinois.
Myers, Elmer E., Brookville Glass and Tile Co., Brookville, Pa.
Roberts, Jane E., Librarian, State University of Iowa, Iowa City, Iowa.
Shaw, L. I., Ph.D., Assistant Chief Chemist, Bureau of Mines, Washington, D. C.

Foreign Associate.

Berland, Louis, 10 Grande Rue, Villejuif, Seine, France.

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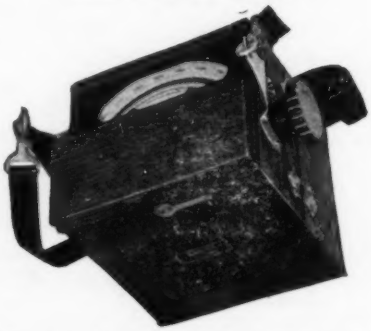

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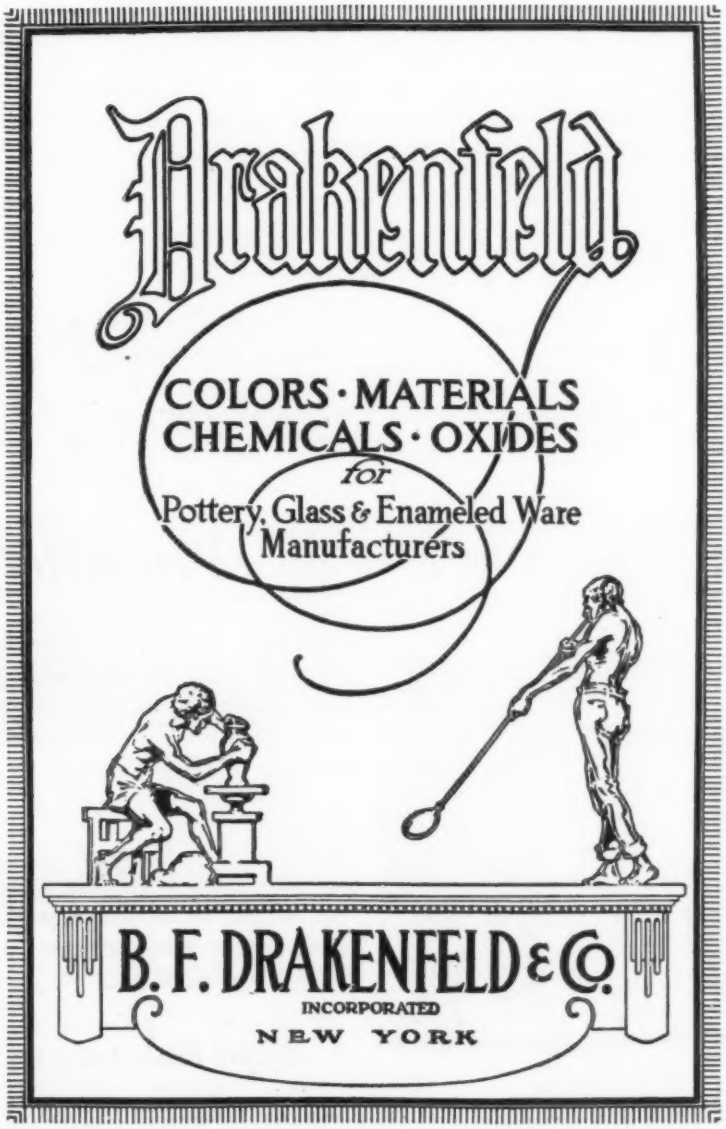
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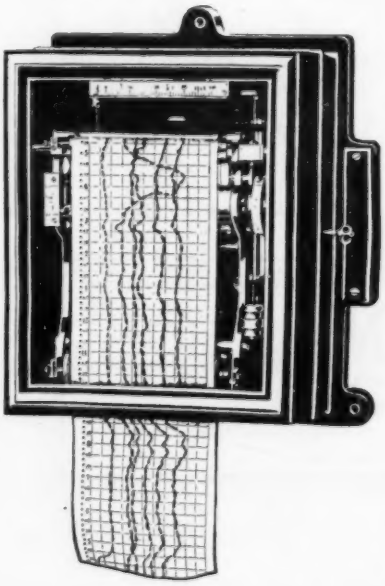

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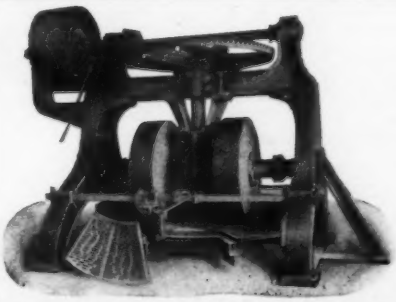

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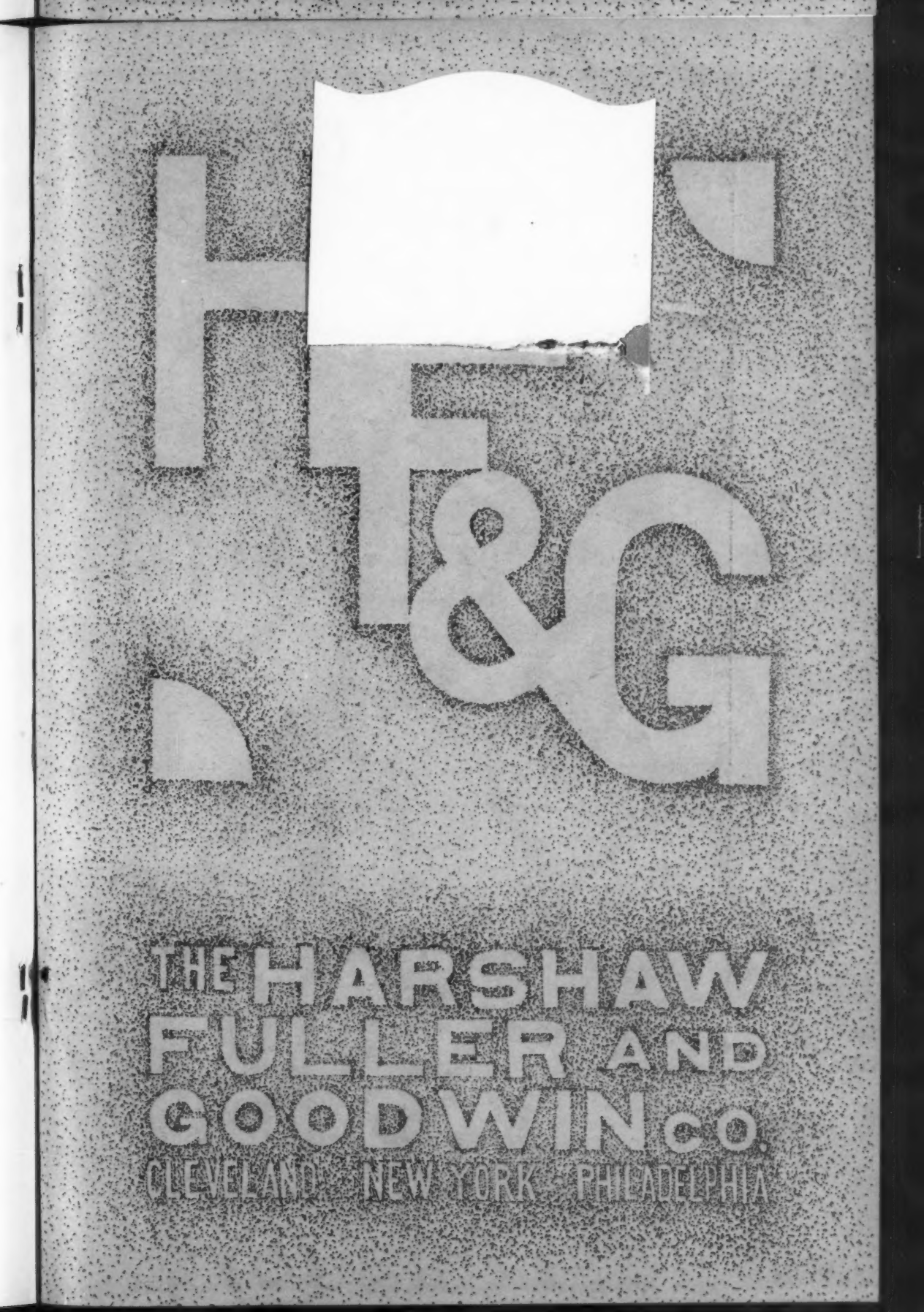
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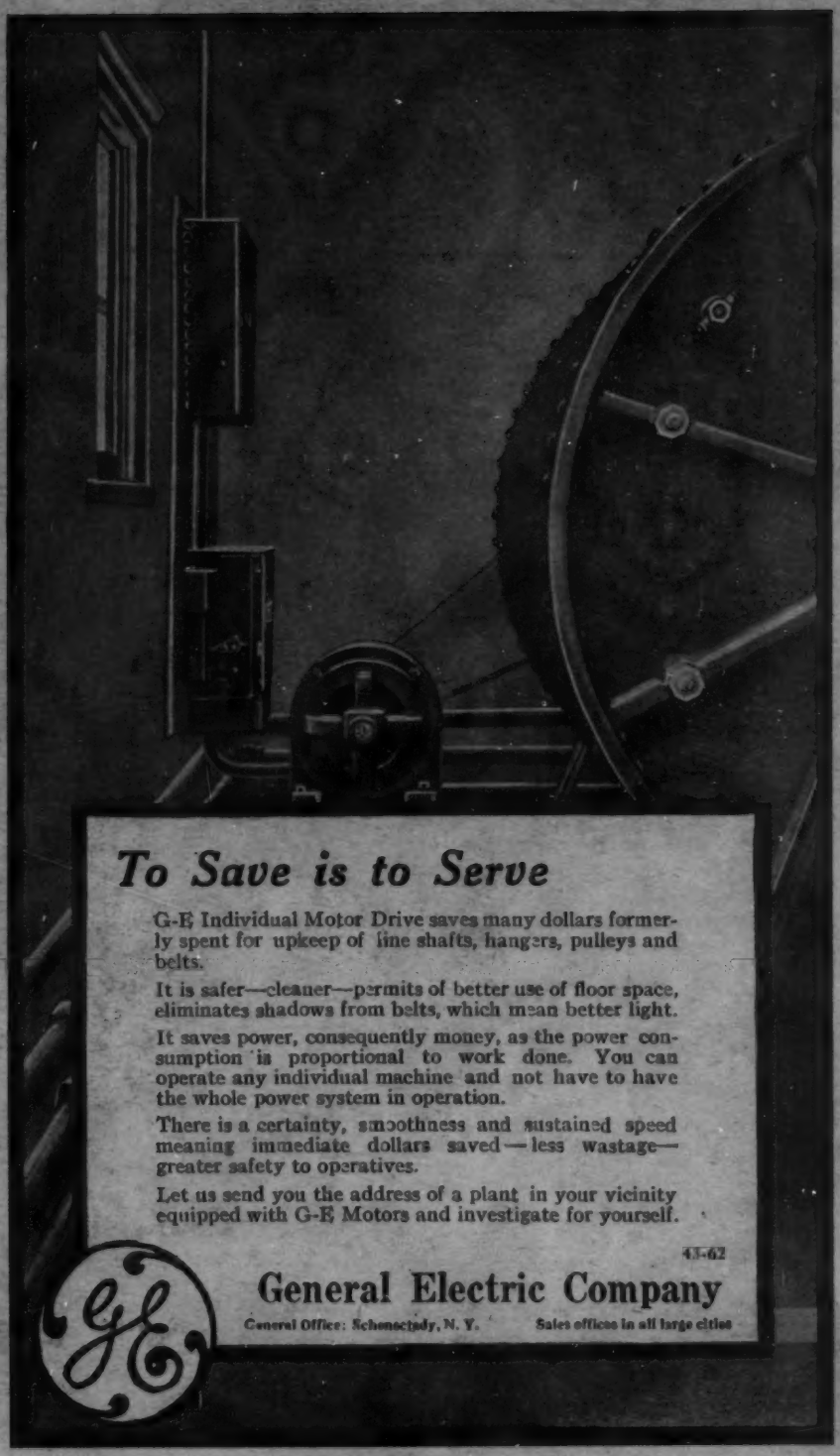

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